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FINAL TECHNICAL REPORT

INVESTIGATION TO OBTAIN NEW FAT DERIVED COMPOUNDS THAT
MIGHT SERVE TO EXPAND OUTLETS FOR SURPLUS ANIMAL FATS

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As animal fats are by-products of the meat industry, control of their production is very difficult, if not impossible, and often unavoidable surplusses require an utilization. Production of chemical derivatives of fatty acids offers the best promise for dealing with the surplus problem.

Of the various type of derivatives obtainable from fats, the production of hydroxy fatty chains appears to be one of the more promising. In fact, with the exception of ricinoleic acid, there are no important commercial natural hydroxylated fatty acids.

Though the production of monohydroxylated and dihydroxylated fatty chains has been extensively studied, there was, before the present researches have been published, very little information on the possibility of obtaining unsaturated hydroxylated fatty chains and branched hydroxylated fatty compounds with the hydroxyl in the secondary chain.

A possible solution of the first point is to transform an unsaturated acid, like oleic acid, in the corresponding allylic hydroxylated one, i.e. to introduce the hydroxyl group on a carbon adjacent to the double bond.

Synthesis of chemically pure compounds showed that two classes of derivatives may be obtained :

- the monohydroxyallylic derivative whose chain is isomeric with the ricinoleic chain,
- the dihydroxydiallylic derivatives which are new compounds.

Different ways of technical preparation have been explored.

The first was the hydrolysis of allylic bromides, which are obtained by reaction of an unsaturated derivative with a specific reagent. Hydrolysis offers no difficulty and purification by fractional crystallization of the rough products is easy. The drawback of the method is the number of successive stages to perform.

Reaction with hydroperoxide, even in carefully controlled conditions, is slow and only partial. Overmore, it is not completely selective as dimers are equally formed.

Use of peresters in place of hydroperoxides gives better results since, though the reaction velocity is always low, as no dimers are formed, hydroxylation yield is higher. Employ of t.butyl perbenzoate gives particularly satisfactory results, and products obtained from oleic acid are easily purified. According to the proportion of the reagent used, one can obtain mixtures of mono- and dihydroxylated chains in various proportions.

Allylic oxidation may also result of the action of some chemical reagents.

Selenium dioxide is a very powerful one and is easily put in reaction in various solvents. But its action is not completely specific and very complex mixtures are formed, including beside the desired allylic alcohols, saturated diols and eventually saturated alcohols and ketones.

Better results are obtained with mercuric acetate. This reagent is very specific and leads only to the formation of monohydroxylated derivatives. Though its reaction mechanism affords scarcely to obtain yields higher than 50%, very simple conditions of use and of purification of the formed products were found, giving easily nearly pure products.

Each kind of reaction was extended to functional terminal derivatives of the oleic chain (alcohol and amine particularly).

The greatest feature of the allylic hydroxylated molecules is their high reactivity. Especially they very easily support elimination reactions, leading to the formation of conjugated polyunsaturated chains.

The production of the hydroxylated branched fatty chain was obtained by oxo synthesis i.e. addition at high temperature under high pressure, in presence of cobalt derivatives, of hydrogen and carbon monoxide upon methyl oleate.

Reaction products are rather complex mixtures of various branched derivatives.

Influence of the different factors (temperature, pressure, proportion of gases, quantity of catalyst) was systematically studied.

Conditions leading to the maximum formation of a given compound especially the hydroxylated branched derivative were determined.

From structural studies it appeared that important isomerisations occur during oxo synthesis. Those isomerisations affect the unsaturated chain before addition of both gases.

Geometrical and positional isomerisations have been set for.

It was shown that in the absence of hydrogen, isomerisation may be obtained without addition on the double bond. A mixture of all the possible isomers of oleic chain, in equal quantity, is then obtained.

Hydroxylated branched stearic acid is a very reactive compound which suffers spontaneous esterification with formation of either estolides or lactones.

P A R T A

ALLYLIC HYDROXYLATION

The practical importance of saturated hydroxylated acids led to the study and development of hydroxylation reactions. On the contrary the possible ways to prepare unsaturated hydroxylated chains have been much less explored for, particularly such reactions appear more tedious. Such a problem may probably be approached from different sides. Since hydrogens of the allylic carbons in a monounsaturated olefin present a particular mobility, specific and limited allylic oxidation of a monounsaturated fatty chain - in our case oleic chain - seems to be relatively easy. The advantages of allylic oxidation is to preserve unsaturation and to fix, at least approximatively, the position of the hydroxyl.

Our researches on that subject may be divided in two general parts :

- Indirect hydroxylation using as starting material allylic brominated derivatives, and substituting the halogen by an hydroxyl,
- Direct hydroxylation with various reagents of different reactivity and specificity : selenium dioxide, mercuric acetate, hydroperoxides and peresters.

I - INDIRECT HYDROXYLATION - HYDROLYSIS OF ALLYLIC BROMIDE

Bromination of methyl oleate or other oleic derivatives with N-bromosuccinimide (NBS) is easy and transfer of halogen is always greater than 95%. Reaction mixtures are complex and contain always four components (1) :

- allylic monobromide - $\text{CHBr} - \text{CH} = \text{CH} - \text{CH}_2 -$
- diallylic dibromide - $\text{CHBr} - \text{CH} = \text{CH} - \text{CHBr} -$
- addition dibromide - $\text{CH}_2 - \text{CHBr} - \text{CHBr} - \text{CH}_2 -$
- unreacted olefin - $\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 -$

Relative proportion of components belongs principally to the molar ratio NBS/oleic chain, the nature (polarity) of oleic derivative used and the quality of NBS.

As both allylic methylenes are equally reactive and as partial transposition occurs during bromination, allylic monobromides are an equimolar mixture of the four possible isomers. As diallylic dibromides are formed from the monobromide without transposition, they are a mixture of 3 isomers, one of them being twice more important than the others two. (2).

In such mixture allylic bromine is very reactive and may be easily replaced, whereas addition bromine is particularly stable.

A - Obtention and characteristics of pure compounds

Knowledge of allylic bromides induce to think that two kinds of hydroxyallylic derivatives are possible :
monohydroxyallylic derivatives with the sequence $-\text{CH}_2-\text{CH}=\text{CH}-\text{CHOH}-$ inside the chain,
dihydroxydiallylic derivatives with the characteristic group $-\text{CHOH}-\text{CH}=\text{CH}-\text{CHOH}-$.

They were obtained from the corresponding bromides through a nucleophilic substitution with a silver salt, followed by a saponification of the intermediary ester.

As pure bromides may not be obtained, since they are too unstable, we used, as starting materials, particular mixtures containing beside one bromide as a main constituent, only traces of the other bromide. These mixtures are :

- the one resulting of the action of 0.5 mole of NBS per fatty chain, which may be considered as a mixture of allylic monobromide and unreacted chain;
- the one resulting of the action of 2 moles of NBS per fatty chain, which is a mixture of the two dibromides.

Nucleophilic substitutions were made either in homogeneous media (acetic solution) using silver acetate, either in heterogeneous media with careful mixing of a chloroformic solution of bromide and an aqueous solution of silver nitrate.

Previous treatments were applied to three different oleic derivatives : methyl oleate, oleyl alcohol acetate, and oleonitrile.

The esters corresponding to the first two were saponified and after decomposition and purification the corresponding mono- and dihydroxylated derivatives of oleic acid and oleyl alcohol were isolated as pure compounds after recrystallization. The esters corresponding to oleonitrile were treated according to Bouveault and Blanc, to be transformed to the mono- and dihydroxylated allylic derivatives of oleylamine.

Analytical characteristics of the obtained products are enlisted in table I.

Derivatives of oleic acid were studied more precisely.

Infrared spectra show an important absorption at 967 cm^{-1} indicating that many, if not all, double bonds are trans. Thin layer chromatography (T.L.C.) on silicic acid/ NO_3Ag plates shows only one spot corresponding to the trans form. Only one stereoisomer is then present.

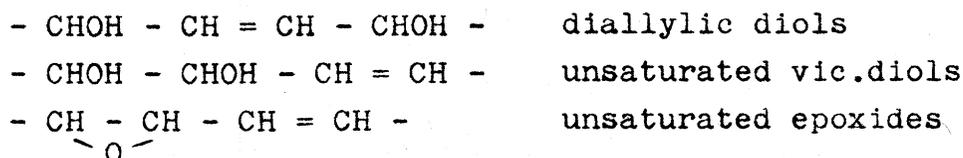
Allylic hydroxyls are easily eliminated through a specific dehydration with p-toluène sulfonic acid in benzene solution. Ultraviolet spectroscopic examination shows that monohydroxyallylic oleic acid

is transformed quantitatively in conjugated dienic acid and dihydroxydiallylic oleic acid in conjugated trienic acid.

Disruptive oxidation with $\text{IO}_4\text{Na} - \text{MnO}_4\text{K}$ according to Jones and Stolp (3), followed by quantitative gas liquid chromatography (G.L.C.) of the mono- and diacid formed, shows that :

the monohydroxylated derivative is (as the bromide) an equimolar mixture of the four possible isomers, and the dihydroxylated derivatives are, as well as the corresponding bromides, a mixture of three isomers.

In view to ascertain that during replacement of bromine in dibromide, to obtain the corresponding diols, no transposition occurs which would lead to the formation either of vicinal diols or epoxides (4)



dihydroxylated diallylic acid was hydrogenated at as low temperature as possible, and in the saturated alcohol obtained, vic.diols or (and) epoxides were researched. No positive answer was found, indicating that no transposition occurs during exchange of bromine of the dibromide.

One must notice that mono- and dihydroxylic allylic derivatives of oleic chain are particularly reactive. Two properties are to be emphasized: the aptitude of the alcohols and their esters to spontaneous elimination when heated above 90°C ; the easiness, even in the cold and in the solid state, of mutual esterification of acid molecules leading to the spontaneous formation of estolides.

B - Hydrolysis of allylic bromide

The use of silver salts is possible for fundamental and exploratory researches, but cannot be in any case a preparative way neither for laboratory purposes nor, of course, for industrial ones.

The lability of bromine in brominated compounds is favourable to hydrolysis reactions.

As starting material, we used the bromination product of oleic acid with equimolar proportion of NBS having the following characteristics :

iodine value :	62.4
total bromine :	22.3%
allylic bromine :	17.2 %

As reference a theoretical hydrolysis of all allylic bromine atoms would give an hydroxylated mixture having the following characteristics :

iodine value :	71.7
hydroxyl value :	139.5

total bromine : 5.9%
allylic bromine : 0

As a conclusion of systematic experiments using aqueous solution of different alkaline salts of various basicity the following hydrolysis procedure was elaborated :

The mixture (121.9g) resulting from the treatment of 100g oleic acid with an equimolar proportion of pure NBS is dissolved in a solution of CO_2NaH (55.5g) in water (330 cm^3). The solution is heated to boiling for 2hrs. After cooling it is acidified and the fatty portion recovered (104.6g). It has the following characteristics :

iodine value : 78.9
hydroxyl value: 130.5
total bromine : 4.8
allylic bromine: 0

After a crystallization at -30° from petroleum ether (10 cm^3 /g) a fraction, bromine free, weighing 61.5g, is recovered (I.V.: 82.5 OH^V.: 189.5).

Alkaline hydrolysis may be extended to non water-soluble or solubilizable derivatives of oleic acid, using a common solvent. The best one in the case is tetrahydrofuran. Hydrolysis being done at 100°C , use of THF requires reaction to be conducted in a pressure vessel. Results obtained summarized on table II are good.

So allylic bromination and hydrolysis of allylic bromides are in the case of oleic acid and of its terminal functional derivatives a satisfactory process to prepare, in a fairly pure state and with a satisfactory yield, hydroxylated allylic oleic acid and derivatives.

II - DIRECT HYDROXYLATION WITH SPECIFIC OXIDIZING REAGENTS

Direct and specific oxidation of unsaturated molecules are well known in organic chemistry. Many reagents have been proposed therefor. Very few of them have been used in lipid chemistry and most often their action is not limited to the formation of α,β -unsaturated alcohols.

Direct oxidation with oxygen followed by reduction of the hydroperoxide in very carefully controlled conditions has been recently investigated by Ault et al (5) and seems to give satisfactory results.

Use of chemical reagent is not without interest if it produces relatively short reaction times and more easily renders the final purification.

For that purpose we successively studied the action of selenium dioxide, mercuric acetate, hydroperoxides, and t.butylperesters.

A - Oxidation with SeO_2

Selenium dioxide is a selective oxidation reagent which gives with olefins, among other products, allylic alcohols. However its ac-

tion is not completely specific and numerous by-products are formed including principally olefinic ketones (7) and saturated alcohols(8).

It has been principally opposed to short chain olefins and terpenes, and relatively few works have been devoted to its application in the field of fats and oils (9,10).

1) Reaction in acetic media

Conditions used for preliminary experiments were those described by Guillemonat (11) : i.e., reaction in boiling acetic solution with a molar defect of SeO_2 .

Chemical and spectrographic examinations of crude products, directly, after saponification and after saponification and dehydration, enabled us to determine the best conditions of reaction. There are the following :

To a solution of oleic acid (1 mole) in acetic acid ($5\text{cm}^3/\text{g}$) heated to 70° is added by successive portions in 4hrs approximatively 0.35 mole of SeO_2 .

After dilution with water the fatty phase, in which every hydroxyl group formed is acetylated, is saponified; a part of the selenium precipitates as red Se during acidification following saponification, and the remaining Se is removed by final treatment with mercury (12).

A typical reaction mixture has the following characteristics :

iodine value :	54.2
hydroxyl value:	137.5

No other functional groups are present.

As shown by results of UV spectrophotometric determinations after dehydration, the main part (43%) of the hydroxyls are in allylic position. Some of the others (9.4%) are associated in vic.diols. UV data after dehydration indicate that allylic alcohols are mixture of monohydroxyallylic and dihydroxydiallylic derivatives. It remains naturally in the mixture at least 30% of unchanged oleic chains.

Changes in operatory conditions give poorer results : higher temperature produces spontaneous elimination of allylic alcohols and formation of conjugated systems; greater proportion of selenium dioxide affords formation of carbonyl groups.

Composition of crude product was determined as follows. The hydroxylated molecules and the non hydroxylated ones were separated by reversed phase partition column chromatography according to Naudet et al (13), and each fraction was analyzed.

The unhydroxylated acids were examined by GLC and found to be essentially octadecenoic acid with a very small quantity of conjugated octadecadienoic acid which is formed from monohydroxyallylic acid during recuperation treatments. Infrared examination and structure de-

termination show that octadecenoic acid is the cis 9.10 isomer, that means untransformed oleic acid.

Examination of the hydroxylated fraction is more complex. Ultra-violet spectroscopic determinations after dehydration confirm the presence of both monohydroxylated and dihydroxylated derivatives. Thin layer chromatography after dehydration of the allylic alcohols shows that monohydroxylated saturated acids are present beside saturated vic diols. Every allylic hydroxyunsaturated acids are trans compounds (by IR and TLC). The monohydroxy are equimolar mixture of four isomers which have yet been characterized. Vic.dihydroxysaturated acid is the 9.10 threo dihydroxystearic acid, and the monohydroxysaturated acid is a mixture of the 9 and 10 isomers of hydroxystearic acid.

Quantitative estimation of each component is possible and the saponified crude mixture has the following composition (in weight) :

allylic hydroxyoctadecenoic acid :	38.3%
diallylic dihydroxyoctadecenoic acid :	5.0%
9(10)hydroxystearic acid :	6.9%
9.10 dihydroxystearic acid :	9.4%
oleic acid :	35.0%
conjugated octadecadienoic acids :	3.6%
palmitic acid :	1.8%

2) Experiments in various solvents

Acetic acid, in spite of the very favourable results it affords, is not very satisfactory : it is expensive, very difficult to handle and to eliminate, and its recuperation is nearly impossible. Overmore, all formed hydroxyl groups are acetylated and obtention of free alcohol-acids needs a saponification treatment. Various examples of SeO_2 oxidation in non acetic media are given in the litterature (14), and so we tried to work in various solvents.

All experiments were performed in the optimal conditions found for oxidation in acetic acid and the results are joined on table III. The following conclusions are to be made :

- in all the tested solvents, oxidation is possible but its velocity differs as, in the devoted reaction time, its yield (i.e. recovery of oxygen from SeO_2 used expressed through the sum : hydroxyl value + carbonyl value $\times 2$) depends of the solvent. It is generally high, but is very low in some cases (pyridine) and sometimes substrate oxidation may be balanced by reaction with the solvent (ethanol).

In every cases when velocity is high, hydroxylation is the main if not the only reaction. Ketonic groups when formed are present in small quantities. No elimination forming unsaturated systems occurs during oxidation.

Catalytic dehydration of reaction mixtures leads to the formation of conjugated dienes in important proportion and also to the formation of trienes, indicating that allylic mono- and dihydroxides are the main components.

In all solvents, in more, saturated adjacent dihydroxides are present.

As shown by table III, quantities of ketone and vicinal diols formed vary with the nature of the solvent. It may be of interest to relate those yields to any characteristics of the solvents. Among those characteristics the dielectric constant gives particularly interesting indications. A plot of dihydroxylation yield and ketone yield against dielectric constant is given on fig.1. The obtained curves make more easy the choice of the solvent.

Reaction in CCl_4 has been particularly studied. As preceedingly done for reaction in acetic acid, nature and structure of formed compounds were determined, and detailed composition calculated.

Here and contrarily to results obtained in acetic media, monohydroxyallylic octadecenoic acids are only a mixture of two isomers : those in which respectively the hydroxyl is located in the 9 or 10 position and the double bond in 10-11 or 8-9 positions, indicating that a complete transposition occurs during the reaction. Dihydroxydiallylic derivatives are the corresponding compounds. Ketones formed are the vinyl unsaturated ones and correspond probably to allylic alcohols. As in acetic acid, unreacted oleic acid has not been isomerised, and vicinal dihydroxy acid is dihydroxystearic acid. No saturated monohydroxy acid is present.

Composition is :

allylic hydroxyoctadecenoic acid :	22.8%
diallylic dihydroxyoctadecenoic acid :	2.3%
9.10 dihydroxystearic acid :	7.9%
cetoctadecenoic acids :	8.1%
oleic acid :	52.5%
conjugated octadecadienoic acids :	4.7%
palmitic acid :	1.7%

3) Oxidation of functional derivatives of oleic acid

SeO_2 oxidation is not limited to oleic acid. Functional derivatives may² also be oxidized in the same conditions. Exemples of such treatments are given in table IV.

In each case utilization of SeO_2 is complete and oxidation yields are good. But as a rule hydroxylation yields are lower, whatever the solvent may be, with functional derivatives than with oleic acid or methyl olate. Oxidation is less selective and more ketones are formed. Terminal functions are generally not altered. However oleylamine, oleonitrile at a very few degree and probably oleyl alcohol are more or less damaged.

4) Mechanism

In view to elucidate a possible mechanism, kinetics studies were done. Their results are summarized in fig. 2. Allylic

hydroxyacids, dihydroxystearic acid and probably monohydroxystearic acid are concurrently formed with different velocities according to the nature of the solvent. Dihydroxydiallylic acids and ketones result of secondary reactions of primarily formed molecules.

A satisfactory mechanism has been elaborated and is summarized on fig. 3.

It takes in account every experimentally made observation concerning as well the structure of the formed compound as well the kinetic results.

5) Discussion

Consequently SeO_2 appears as a very powerful reagent. Its use is easy, and oxidation yields are good. But complex mixtures are obtained containing beside the looked for molecules, many undesirable while less or unreactive compounds. Purification of reaction products is rather tedious and gives no sufficiently satisfactory results.

B - Oxidation with mercuric acetate

Mercuric acetate $((\text{CH}_3\text{COO})_2\text{Hg})$ gives with olefins numerous reactions. Besides its addition to double bonds (oximercuration)(15), its employ as allylic oxidative reagent has been set for by numerous workers (16), especially Rappoport et al (17). Excluding a tentative but only partial work of Takaoka and Toyama (18), that sight of the problem has not been examined in lipid chemistry. Nevertheless, as will show the following results, mercuric acetate is a particularly interesting allylic oxidative reagent when opposed to the oleic chain.

1) Reaction in acetic media

At first, we worked in acetic acid solution as recommended by Toyama and Takaoka using equimolar proportions of the reagent. A systematic search of the best operating conditions led us to the following :

To an acetic solution of methyl oleate ($5\text{cm}^3/\text{g}$) add an equimolar quantity of mercuric acetate and heat the mixture to 90°C . In the first minutes of heating $(\text{CH}_3\text{COO})_2\text{Hg}$ dissolves itself. After nearly half an hour, a white precipitate appears; after $2\text{h}.1/2$ it progressively turns to metallic mercury. After 14hrs reaction is stopped; the solution is water diluted and the fatty portion recovered as usual. Spectrographic IR examination and chemical investigations show it contains principally acetate of allylic hydroxyesters and that no other functional derivatives are present. After saponification the acid mixture is analyzed and the structure of the different present components determined. It is essentially a mixture of allylic hydroxyoctadecenoic acid and octadecenoic acid.

Allylic hydroxy derivatives are nearly exclusively trans mono-substituted ones. They are an equimolar mixture of the four possible isomers corresponding to an equal attack with partial transposition of both allylic methylenes.

Octadecenoic acids are a mixture of both geometrical isomers, nearly in proportion 2 trans/1 cis without any displacement of the double bond along the chain.

Ponderal composition after saponification is :

allylic hydroxyoctadecenoic acid :	59.5%
diallylic dihydroxyoctadecenoic acid :	1.6%
octadecenoic acid (<u>cis</u> and <u>trans</u>) :	38.9%

Changes in operatory conditions do not afford important composition variations. Lengthening the reaction time until 50hrs increases the hydroxylated acid yield to 80% only, and using two moles of mercuric acetate per mole of methyl oleate has no effect at equal reaction time.

2) Reactions in other media

As for SeO_2 , oxidations were effected also in various solvents. Results are reported on table V.

They are very different between a solvent and another and reason of such differences will clearly appear after discussion of mechanism.

In some solvents no reaction occurs. In some others, addition of the reagent seems to be the main phenomenon, and in others, like dioxan, allylic oxidation occurs.

The reaction in that last solvent was more precisely studied.

Fatty products formed are the same as in acetic acid. Before saponification, all hydroxyl groups are acetylated, and the saponified product is essentially a mixture of trans hydroxyallylic octadecenoic acids (4 isomers in equal proportion) and partially stereoisomerized octadecenoic acid.

Significative differences are to be noted with reaction in acetic media :

- in dioxan, metallic mercury does not appear and the white precipitate remains unchanged during all the reaction. It has been characterized as mercurous acetate $(\text{CH}_3\text{COO})_2\text{Hg}_2$.
- using equimolar proportions, after 14hrs yield of allylic hydroxide reaches only 50%. Lengthening the reaction time does not increase it.
- using 2 moles of mercuric acetate per mole of methyl oleate does not give better result after 14hrs. but enables to obtain more than 75% yield (on a molar basis) after 50hrs.

3) Kinetic study and mechanism

In view to elucidate the possible mechanism, reaction studies, in which concentration variations of all components were followed, were done as well in acetic acid as in dioxan. Results obtained are summarized on fig. 4 and 5.

From that results the following mechanisms may be set for (fig.6)

In a first time an equimolar dimeric adduct between mercuric acetate and methyl oleate is formed. That adduct later decomposes, giving a mole of partially isomerized methyl octadecenoate, and a mole of an organomercuric compound which may decompose to mercurous acetate and acetylated methyl allylic hydroxyoctadecenoate.

In acetic acid, dismutation of mercurous acetate occurs, forming metallic mercury and regenerating mercuric acetate.

As in the dimeric adduct, if sufficient proportion of mercuric acetate is present, all the methyl oleate is included, the limiting factor for the development of the reaction is not mercuric acetate, but methyl oleate. When an excess of mercuric acetate is present, it can react only when methyl octadecanoate has been liberated from the adduct.

As formation and decomposition of that adduct is essential for the advancement of the reaction, influence of the polarity of the solvent on both stages was investigated.

It was shown that adduct formation is very easy and total in non polar solvents like CCl_4 and benzene, and its decomposition is all the more rapid the solvent is more polar.

This suggests that best conditions of use will be a two stages reaction : formation of the adduct in an apolar solvent, followed by decomposition of this in a polar solvent. But in that case, on the contrary to what occurs in acetic acid, the yield would be limited to 50% on a molar basis.

4) Oxidation of functional derivatives

Functional derivatives were treated with mercuric acetate comparatively with methyl oleate. Results are reported on table VI.

In each case hydroxylation yields are good. As a rule they are significantly lower than for methyl oleate. Terminal functions are not altered, but alcohol is completely, and amine partially, acetylated.

5) Discussion

From preceding results, mercuric acetate appears as a particularly interesting reagent.

Though in the most easier conditions of use, it does not afford a molar hydroxylation yield higher than 50%, it is a very specific reagent since it leads only in practise to the formation of α,β -unsaturated monoalcohols. A typical way to obtain allylic hydroxyoctadecenoic acid may be the following : equimolar quantities of oleic acid and mercuric acetate are reacted in CCl_4 for 30 minutes at boiling point, solvent is evaporated, and residue is dissolved in ethyl oxide and the solution heated to boiling for 14hrs. After filtration to separate mercurous

acetate, the solution is cooled at low temperature and the elaidic acid separated by crystallization. The filtrate is evaporated and the residue saponified. The crude hydroxyoctadecenoic acids are recovered as usual and may be purified by a complementary crystallization

C - Oxidation with peresters and hydroperoxides

Esters of peralcohols (19) are used from long ago as specific oxidants for allylic carbons, but no application of this reaction has been proposed in lipid chemistry.

After preliminary experiments the best conditions of reaction were determined and may be summarized as follows.

To a solution of methyl oleate in a convenient solvent, containing Cu^+ ions as indicated by Kochi et al. (20) is added the desired proportion of perester or hydroperoxide. The mixture is then heated for several hours at 90° under nitrogen with constant agitation.

The following observations were made :

- whatever will be the reagent, the solvent or the concentration of the solution, reaction is very slow and its velocity decreases gradually, probably as a consequence of the dilution of the reagents.

In every cases, after 30hrs, oxidizing agent has only been partially utilized.

Hydroxylation yields consequently are low and do not surpasses for equimolar proportion of reagent : with peresters 60-70%, and with hydroperoxide 35-40%.

- whatever will be the reagent, the oxidation is very specific as only allylic hydroxides are formed, excluding all other oxygenated derivatives (ketone, saturated alcohols).

- in acetic acid acetates are always obtained.

- in non reactive solvents : with peresters, allylic hydroxyles are esterified by the acid moiety of the reagent (acetate with peracetate benzoate with perbenzoate),

with hydroperoxides : free alcohols are obtained.

- with peresters no dimers are formed; with hydroperoxide an important formation of dimers occurs.

Structure of the formed products has been determined.

Allylic hydroxides are mixture of mono- and dihydroxylated derivatives. The former are an equimolar mixture of the 4 possible isomers. The untransformed octadecenoic acid is partially stereoisomerized (# 2 trans/1 cis) but did not suffered any positional isomerisation).

The exact structure of the dimer formed with hydroperoxides is yet being studied. There are good reasons to think it may be a dehydro-dimer, but this point must be confirmed.

Use of peresters may induce a rather simple way for preparing technical hydroxy acids : oxidation of oleic acid is performed during 30hrs at 90°C for exemple with t.butyl-perbenzoate in acetic acid. After cooling and dilution, the fatty portion is recovered and water-washed; then it is dissolved in petroleum ether and the elaidic acid (nearly 2/3 of the unoxidized fraction) is discarded through crystallization. The filtrate is evaporated, then saponified, the crude hydroxylated acid may be further purified through crystallization.

In conclusion one may say that oxidations with peresters are satisfactory; though their yields are low, since the reagent is only partially utilized, they are very specific and lead to mixture of mono- and dihydroxyoctadecenoic acid, the proportion of which is a function of the molar ratio oleic acid/reagent.

The use of hydroperoxides, though it may prevent in some cases the formation of esterified derivatives, affords no advantages, since the yields are lower than with peresters, and in more partial dimerization occurs.

P A R T B

OXONATION REACTION

The reactivity of a functional group belongs to the nature of the carbon atom to which it is bound : from such a point of view, reactivities of hydroxyl groups are characteristic.

Classical addition reactions on the double bond of monounsaturated acids or esters result in the formation of a secondary functional group. So the bi- or multifunctional obtained molecule contains in the same time functional groups, bound to primary (the terminal one) and secondary (the middle chain one) carbons. Synthesis of branched multifunctional derivatives in which the various identical or not functions are bound in the branched chain to primary carbon consequently offers a non neglectable interest.

Such molecules may be obtained by adding, on double bonds, various monocarbon compounds : application of Ritter's, Prins', Koch's reactions to fatty compounds have yet been studied (21, 22, 23).

Oxonation reactions result also, and frequently more easily and more rapidly than others, in the formation of primary branched functional derivatives.

Essentially they consist to add to an olefin under convenient temperature and pressure conditions, in presence of multivalent metals as Co, Fe, Ni, carbon monoxide and an other reagent (H_2 , H_2O , CH_3OH , NH_3).

Oxo synthesis - or more exactly hydroformylation - is the most important form of use of oxonation reaction. Well known and largely used in petroleochemistry, it is nearly unknown in lipid chemistry where only few experiments were done (24 à 27). Though generally short chain and terminal olefins are used, no special difficulties seem to be awaited when long chain, symetric olefins are used, except perhaps the decrease in reactivity and the possibility of important isomerisations.

Study of methyl oleate hydroformylation is presented in the present report.

A - Operatory conditions

Assays were performed in the apparatus shown on figure 7.

A stainless steel, 125 cm³ capacity, autoclave, able to suffer high temperature and high pressure (up to 300°C and 300kg/cm²) is located in an electrical heater, sideways swinged. Temperature may be regulated, when desired value is obtained, to $\pm 2.5^\circ C$. A convenient device enables to introduce before operating, at the desired pressure, necessary gases from commercial bottles. Pressure is controlled with

a manometer to the nearest kg/cm².

The processing of an operation is the following : 20g of methyl oleate (98% purity free from polyunsaturated esters) and the desired quantity of the chosen cobalt salt are placed in the autoclave. After this one has been closed, it is filled to 60kg/cm² successively, to displace air, with hydrogen, carbon monoxide and hydrogen. Convenient partial pressure of CO is then established and needed initial total pressure reached with H₂. Heating and agitation are put in operation. During temperature runs up, pressure increases. When selected temperature is reached, pressure becomes constant during a more or less important time (induction period) then begins to decrease first rapidly, then slowly until a minimal value.

When pressure does not significantly decrease, agitation is stopped, and the autoclave is rapidly cooled in a water bath. After decompression and displacement of gases with nitrogen, it is opened and its content is quantitatively recovered with a convenient solvent.

The solution is then acid treated to promote decomposition of the catalyst, and after washing and drying, solvent is evaporated and fatty portion analyzed.

B - Study of the reaction mixtures

Fresh, non acid treated solutions of oxonation products are brown. Their infrared spectra contain two doublets located at 2068 - 2020cm⁻¹ and 1869 - 1834cm⁻¹ which, according to Kirch and Orchin(28) are characteristic of the cobalt carbonyls Co₂(CO)₈ and HCo(CO)₄,⁻¹ active forms of the catalyst. In the same spectra peaks at 2660cm⁻¹ and 3330cm⁻¹ respectively owing to aldehyde and hydroxyl groups are present. If the ethereal solution is kept over night in the refrigerator before acidic treatment, it becomes green and characteristic doublets of carbonyl compounds disappear from the infrared spectra.

From the determination of the analytical values on the acid treated mixture (a typical example is given in table VII), the following statements are possible.

- unsaturation has completely disappeared
 - ester linkages are always present
 - aldehyde groups have been formed
- In more - free acid groups are present (excluding eventually the acidity brought by the fatty moiety of the catalyst generator).
- free hydroxyl groups are also present.

These results induce to the conclusion that the composition of the reaction mixture is rather complicated and that the awaited methyl formylstearate (1) (aldehyde ester) is accompanied at least by methyl hydroxymethyl-stearate (2) (alcohol ester) and methyl carboxymethyl-stearate (3) (acid ester).

using, according to (29), oxalic acid in ethereal solution.

D - Nature of the cobalt salt used

Catalysts for oxo synthesis are cobalt carbonyls, more specially dicobaltoctacarbonyl which is probably reversibly transformed during reaction in cobalt tetracarbonylhydride.

Dicobaltoctacarbonyl which may be either formed in situ or prepared, results of the decomposition of a cobalt salt under pressure of CO and H₂ at elevated temperature. Nature of the cobalt salt is not unimportant.

Salts of cobalt and mineral acids including cobalt carbonate are not sufficiently reactive. Salts of organic acids seem to be preferred; especially salts of aliphatic acids led very easily to a very active catalyst. Salts of fatty acid present the advantage to be very soluble in a fatty phase, but the free acid which appears during formation of the catalyst remains in the reactive mixture.

Cobalt acetate, though very hygroscopic, is to be preferred, since acetic acid is easily eliminated during washing.

Preformed according to Wender et al. (30) dicobaltoctacarbonyl has the advantage to suppress inhibition period and to enable reaction at lower temperature, but elimination of cobalt is more tedious than with in situ formed catalyst.

E - Influence of various factors on oxosynthesis

Many factors may influence not only reaction velocity but also composition of the obtained product. Among those the most important seemed for us to be : initial pressure, temperature, relative proportion of CO and H₂, catalyst quantity. Results obtained are discussed below.

1) Influence of pressure - Isothermal reactions

In those experiments temperature, partial pressure of gases, quantity of metallic Co (150°C - $P_{H_2} = P_{CO}$ - 1% Co by weight) were kept constant. Initial pressure was increased from 80 to 180 kg/cm² by 20kg/cm² each time.

Pressure variations were followed during each experiment, and the related curves are reported on fig. 8. It is easy to notice that increasing initial pressure decreases in a very noticeable manner the reaction time, especially the inhibition period.

Calculated compositions are reported on table IX. No significant differences are to be noted. Percentage of methyl stearate and alcohol esters are nearly constant. No estolides are formed. Some concomitant variations are noted for the respective percentage of aldehyde ester and acid ester, but the partial sum of these two compound is nearly constant.

As conclusion, if pressure exercises a marked influence upon reaction velocity, it has no influence on the composition of the final product.

2) Influence of temperature - Isobaric experiments

In these experiments initial and partial pressures and Co proportion were kept constant ($160\text{kg/cm}^2 - p_{\text{H}_2} = p_{\text{CO}} - 1\% \text{ Co}$) and temperature increased by 10°C from 110°C to 190°C .

As shown by curves of fig. 9 low temperature gives very long time of reaction which progressively decreases when temperature increases. The decrease of reaction time depends principally of the diminution of inhibition period, but as shown on fig. 10 when preformed cobalt carbonyl is used, lowering the temperature decreases also the true reaction time. Inhibition period disappears at 170°C . Compositions are reported on table X. They vary greatly from an assay to the other; at 130° (using preformed catalyst) or at 150° (using catalyst in situ generated) percentages of alcohol esters and methyl stearate are low. The main components are aldehyde esters and acid esters. No estolides are formed.

Increasing temperature makes yield of aldehyde ester, acid ester and methyl stearate lower, whereas alcohol esters and estolides increase. At 190° they represent more than 80% of the total.

3) Influence of partial pressure of gases

Relative molecular proportion of gases-related to partial pressure of each of them-has to be considered.

For such a purpose experiments were performed under constant initial pressure (150kg/cm^2) at two temperatures (150°C and 190°C) with a constant proportion of cobalt (1%) and with different partial pressures always kept in a simple proportion ($4/1 - 2/1 - 1/1 - 1/2 - 1/4$).

Composition of final products are reported on table XI. At both temperatures, variation of relative proportions of gases modifies more or less the compositions.

At 150° a relatively low excess of carbon monoxide has no significant influence, but, if a too great excess is used, reaction is not complete. An excess of hydrogen has a reductive effect. More methyl stearate is formed and upon all aldehyde esters are partially transformed in alcohol esters.

At 190° also a considerable excess of CO leads to an uncomplete reaction and more aldehyde esters are formed. An excess of hydrogen, on the contrary, has no influence on the composition but if a very large excess is used, the catalyst is reduced and after reaction metallic cobalt is present in the reactor.

4) Influence of catalyst proportion

In view to investigate the influence of the quantity of catalyst, experiments were performed as well at 150°C as at 190° (initial pressure : 160kg/cm²) with proportion of cobalt varying from 0.1 to 2% by weight. Results are reported on table XII .

Whatever will be the temperature, the whole reaction time is all the most shorter than cobalt proportion is higher. But in every cases, the inhibition time is, at a given temperature, constant. In consequence one may think that the true catalyst formation velocity is independent of the quantity of cobalt but that the velocity of the reaction itself depends of that quantity.

Composition of obtained products led to the following remarks :

- Proportion of methyl stearate does not significantly vary.
- As well at 150° as at 190° when cobalt quantity increases, the proportion of aldehyde esters (+ acid esters) decreases while that of alcohol esters (eventually estolides) increases.

5) Influence of solvents

Some authors report experiments in solvent media (29). Assays performed as well in benzene as in ethyl oxide did not give significative results. Compositions are nearly constant. It is only necessary to note that the presence of solvent considerably delays the reaction.

F - Kinetic studies

In order to state with precision at what moment the various branched functions appear, kinetic studies are necessary.

They were performed in the following conditions : successive reactions, in usual conditions, were stopped after various times as indicated on curves from fig. 11. Obtained products were recovered and analyzed as usual. Variations of concentration of various components are reported on fig. 12.

a) Kinetic at 150°

The first assay has been stopped just when the maximal pressure has been reached. Cobalt salt is not yet transformed and no reaction occurred.

For the other assays the reaction time is longer. In each of them (Co)₂(CO)₈ has been characterized. Complete disappearance of cobalt acetate needs a rather long time.

Branched functional groups and methyl stearate appear immediately just when cobalt carbonyl is formed and their concentration increases progressively. Aldehyde esters seem to be formed first and some of them transformed in alcohol esters.

b) Kinetic at 190°

Here, reaction begins before the maximal pressure has been reached.

As preceedingly, aldehyde esters are formed rapidly while the other components appear more slowly.

At a given time, all the methyl oleate has been utilized, but reaction go on and aldehyde esters are progressively transformed in alcohol esters while estolides are formed.

G - Isomerisation

Complexity of gas chromatograms induced rapidly to the conclusion that each component of reaction products is by himself a complex mixture of isomers. Trials for isolation of pure compounds which are at present performed in our laboratory confirmed that opinion, since beside branched in the middle of the chain molecules, α, ω bifunctional derivatives were isolated.

One may ask if isomerisation concerns the unreacted olefin or the branched molecules. Methyl oleate was heated under convenient conditions with a cobalt compound in the absence of one or both reactive gases and the products studied for their content of geometrical isomers, from IR data, and positional ones, according to Jones and Stolp.

Using $\text{Co}_2(\text{CO})_8$ as cobalt compound, one may note :

- under H_2 , total hydrogenation
- under CO or N_2 : small but significative decrease of unsaturation.
- under both last gases : stereoisomerisation and positional isomerisation.
- at 150° : isomerisations are more important under N_2 than under CO.
- at 190° : isomerisations are equivalent under both gases.

A particular interest must be given to positional isomerisation. Double bound migrates all along the chain and reaches the extremity of it, as methyl 17-octadecenoate and methyl 2-octadecenoate are formed. When positional isomerisation is complete, the double bound is regularly distributed all along the chain.

Cobalt acetate produces only isomerisation at 190° under CO.

Cobalt tetracarbonyl hydride also produces isomerisation even at low temperature (25°C) while it is transformed in dicobalt octacarbonyl.

Assays performed for kinetic studies were also studied. Untransformed methyl oleate was separated from branched chains by column chromatography and studied. In every cases one notes that when cobalt octacarbonyl is present, isomerisations occur, and that isomerisations - both geometrical and positional ones - are very rapid and precede the addition reaction.

DISCUSSION

The above results may lead to the following conclusion :
Oxo synthesis may be very easily performed using monounsaturated fatty esters or acids as substrates.

The best form of introduction of cobalt to act as catalyst is cobalt acetate. Use of preformed cobalt carbonyl seems at least to be unuseful, and sometimes affords difficulties.

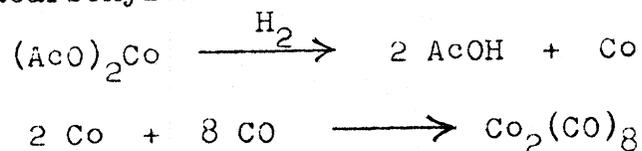
Elimination of cobalt is an important step in the reaction procedure. The best way is to operate in homogeneous solution, for choice with oxalic acid in ethereal solution.

Complex mixtures are always obtained, but a selection of the most convenient operatory conditions enables to form preferably one compound : Aldehyde ester - which may be very easily transformed in acid ester - is the major component when reaction is performed at a relatively low temperature (150°), with a relative excess of CO (2/1) and a small proportion of cobalt (0.2 to 0.5%).

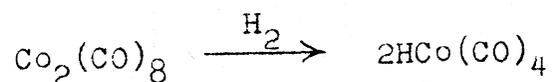
Alcohol esters are, for their part, more easily reached - mixed with estolides - at high temperature (190°), excess of hydrogen (2/1) and high quantity of cobalt (2%).

From the above results a theoretical interpretation of the oxo-nation reaction may be given.

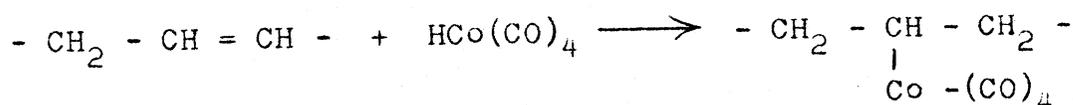
The first step is the formation, from the cobalt salt, of stable dicobaltoctacarbonyl :



This compound is probably transformed in cobalt-tetracarbonyl hydride



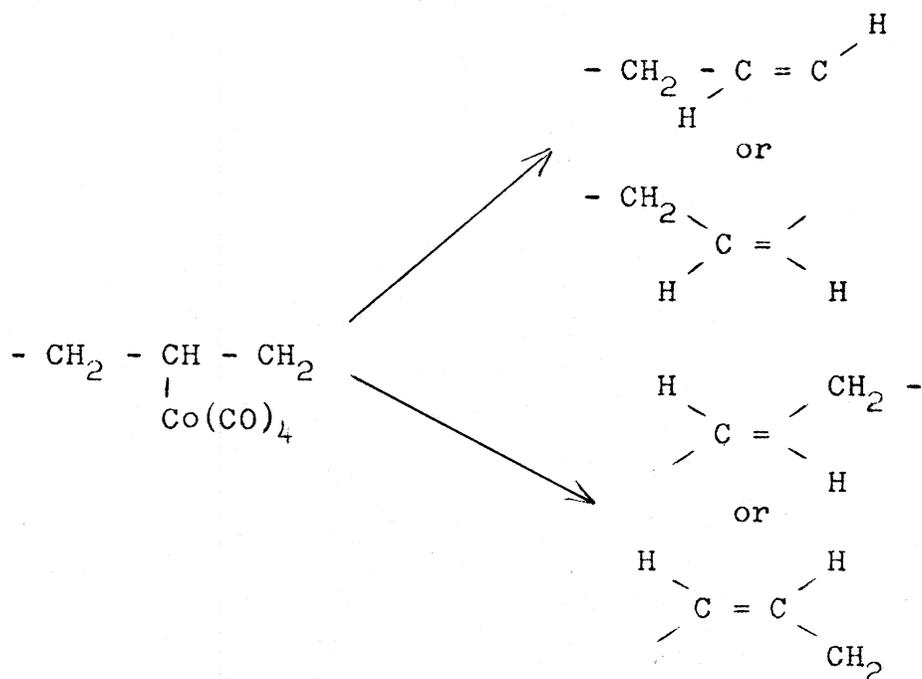
This one, which must be considered as the true catalyst, gives with an olefinic chain an alkyl-cobaltcarbonyl :



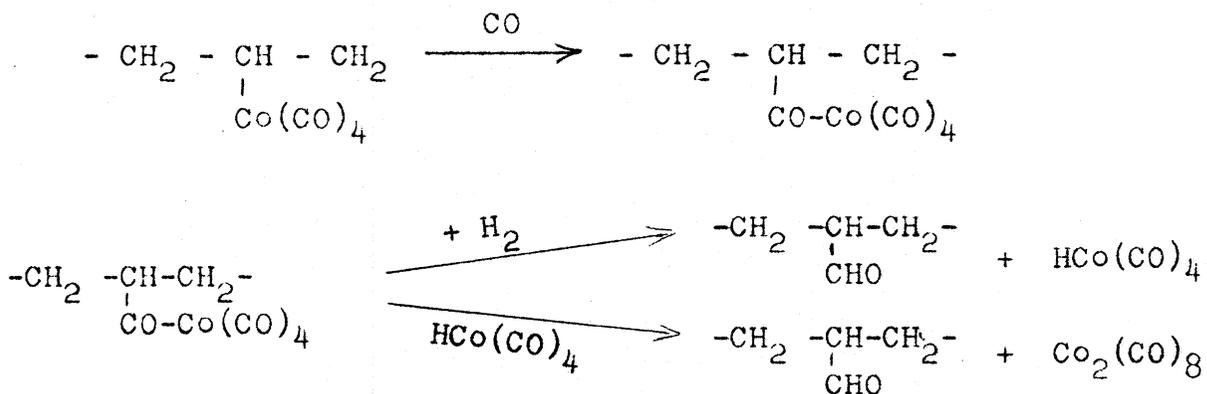
The alkyl-cobaltcarbonyl may react in various ways with different velocity.

a) It may lose, probably very easily, a mole of cobalt-tetracarbonyl hydride, with regeneration of a double bond. Elimination of $\text{HCo}(\text{CO})_4$

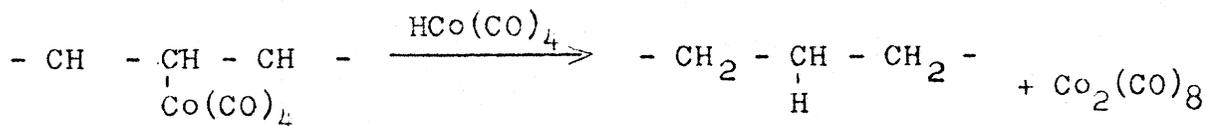
produces isomerisation (positional and geometric)



b) The alkyl-cobaltcarbonyl may react with carbon monoxide to give an acyl-cobaltcarbonyl, which will be, in an other step, reduce either by H_2 , either and more probably by $\text{HCo}(\text{CO})_4$ giving the branched aldehydes :

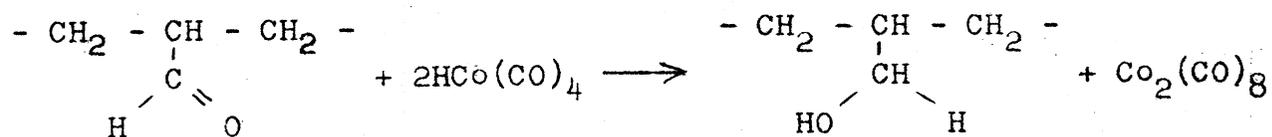


c) Hydrogenation of the double bond may be explained by direct action of $\text{HCo}(\text{CO})_4$ on the alkyl-cobaltcarbonyl



d) Formation of the branched alcohol may result either from a direct

reduction of the aldehyde group, or more probably, from the action of $\text{HCo}(\text{CO})_4$ on that functional group



At the end of the grant, grantee's laboratory perseveres in studying hydroformylation of methyl oleate.

Especially obtention of pure compounds : diacid, aldehyd-acid, and alcohol-acid, is under examination in view to elucidate their different physical and chemical properties.

It is hoped to be able in the future to enlarge the field of the researches concerning oxonation, by substituting to hydrogen other gases to obtain new compounds.

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LIST of PUBLICATIONS

PART A -

- SUR L'OBTENTION DE DERIVES HYDROXYLES ALLYLIQUES DES CHAINES GRASSES MONOINSATUREES.
 - I. Hydrolyse des bromures allyliques
M. Naudet, E. Ucciani et A. Peretz
Rev. Franç. Corps Gras 11, 247 (1964)
 - II. Oxydation par l'anhydride sélénieux
A. Tubul-Peretz, M. Naudet et E. Ucciani
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 - III. Oxydation par l'acétate mercurique
A. Tubul, E. Ucciani et M. Naudet
Rev. Franç. Corps Gras 14, 13 (1967)
 - IV. Oxydation par les hydroperoxydes et les peresters
A. Tubul et M. Naudet
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- Sur quelques dérivés hydroxylés allyliques de la chaîne octadécénique
M. Naudet, A. Peretz et E. Ucciani
Bull. Soc. Chim. (1964) p. 1858
- Sur la structure des produits formés au cours de l'action de SeO_2 sur l'acide oléique
A. Tubul-Peretz, E. Ucciani et M. Naudet
Bull. Soc. Chim. (1966) p. 2331
- Sur l'oxydation de l'oléate de méthyle par l'acétate mercurique
A. Tubul, E. Ucciani et M. Naudet
Bull. Soc. Chim. (1967) p. 464

PART B -

- La synthèse oxo en lipochimie
 - 1) Etude préliminaire de l'hydroformylation de l'oléate de méthyle
R. Laï, M. Naudet et E. Ucciani
Revue Franç. Corps Gras 13, 737 (1966)
 - 2) Etude complémentaire de l'hydroformylation de l'oléate de méthyle
R. Laï, E. Ucciani et M. Naudet
Rev. Franç. Corps Gras (to be published)
- Sur la structure des produits formés au cours de l'hydroformylation de l'oléate de méthyle
R. Laï, A. Bonfand, E. Ucciani et M. Naudet
Bull. Soc. Chim. (to be published)

T A B L E I

Characteristics of the hydroxy allylic oleic derivatives obtained

	Fusion °C	Hydroxyl value		Iodine value (Kaufmann)		Acid value		Nitrogen (g%)	
		Found	Theoretical	Found	Theoretical	Found	Theoretical	Found	Theoretical
Monohydroxy allylic oleic acid	37,5	182	188	85,8	86,2	188	188	-	-
Dihydroxy allylic oleic acid	77,8	356	359	83,2	81,4	179,5	180,5	-	-
Monohydroxy allylic oleyl alcohol	38,2	380	386	88,5	89,6	-	-	-	-
Dihydroxy allylic oleyl alcohol	42,5	547	560	86,2	85,1	-	-	-	-
Monohydroxy allylic oleyl amine	71,5	317*	332	92,0	90,8	-	-	4,75	4,88
Dihydroxy allylic oleyl amine	73,6	468*	503	85,6	84,5	-	-	4,45	4,68

* Corrected for partial reaction of amine group in analytical conditions used (nearly 70% for oleyl amine).

TABLE II

Hydrolysis of crude allylic bromooctadecenic compounds

(HCO₃Na : 4 N - 100°C - in T. H. F. 5 cm³/g)

Compound	Hydrolysis time (h.)	Analytical results		Hydroxylation yield %
		Total bromine %	Hydroxyl value	
Methyl ester	4.5	2.2	141.5	84.5
Alcohol acetate	4.5	3.2	118.3	82.6
Nitrile	3	3.0	139.0	83.0

TABLE III

SeO₂ oxidation of oleic acid in solvents
 (70°C - 4hrs - 0.35 mole SeO₂/mole acid - solvent : 6 cm³/g)

Solvent nature	Di-electric constant	A n a l y t i c a l v a l u e s						Yields	
		Iodine value	Total hydroxyl value	Carbo-nyl value	α-diols hydroxyl value	UV data after dehydration		SeO ₂ utilization	Allylic hydroxylation
						at 232 mμ	at 268 mμ		
Carbon tetrachloride	2.24	60.8	87.9	15.5	38.1	327	69	89.5	38.5
Benzene	2.28	64.4	87.9	24.0	44.8	310	83	100.0	33.3
Toluene	2.38	60.5	87.9	16.7	42.6	330	65	90.5	37.5
Chloroforme	4.81	52.9	107.6	12.0	25.0	402	38	98.0	41.8
Ethyl acetate	6.02	60.2	104.1	0.0	19.4	396	41	77.8	53.1
Acetic acid	6.15	59.6	131.2	0.0	20.4	490	46	98.5	53.6
Tetrahydrofuran	7.40	65.7	90.1	7.1	20.3	321	56	78.5	44.0
Pyridine	12.30	69.4	29.1	0.0	19.9	83	15	21.8	25.9
Acetic acid/acetic anhydrid	14.80	51.5	137.5	0.0	34.0	460	91	100.0	54.8
t. butanol	18.70	64.1	114.2	0.0	36.9	372	49	85.8	45.3
Ethanol	24.70	76.8	68.4	0.0	16.6	205	41	51.4	44.3
Dimethyl formamide	37.00	66.6	96.9	0.0	43.5	212	59	72.5	34.5

TABLE IV

SeO₂ oxidation of functional derivatives of oleic chain

(temperature : 70°C - molar ratio SeO₂/fatty chain = 0.35 - concentration solvent/fatty chain = 6cm³/g)

terminal group	solvent	reaction time (h)	iodine value	total hydroxyl value	carbo-nyl value	Analytical values (※)		α diols hydroxyl value	UV data after dehydration(E ₁) at 232mμ	at 268mμ	hydroxylation yield	oxidation yield	relative hydroxylatio yield
						hydroxyl value	carbo-nyl value						
-COOH	acetic media CCl ₄	4	52.0	137.0	0	34.0	460	91	100.0	100.0	100.0	100.0	100.0
-COOCH ₃	acetic media CCl ₄	4	51.0	131.0	0	33.0	455	75	98.4	100.0	100.0	100.0	98.4
-CH ₂ OH	acetic media CCl ₄	7	59.5	81.5	18.5	38.5	262	56	64.6	86.0	86.0	86.0	75.2
+CH ₂ OCOCH ₃	acetic media CCl ₄	7	57.5	289.0	14.0	29.5	334	61	66.7	95.5	95.5	95.5	70.0
	acetic media CCl ₄		67.0	258.0	28.5	29.0	258	39	44.3	91.8	91.8	91.8	48.3
	acetic media CCl ₄		55.4	300.0	13.0	38.0	490	38	74.7	100.0	100.0	100.0	74.7
	acetic media CCl ₄		57.0	77.0	35.0	37.5	256	84	64.0	100.0	100.0	100.0	64.0
	acetic media CCl ₄		65.0	179.5	44.5	31.5	470	104	-	-	-	-	-
-CH ₂ NH ₂ (**)	acetic media CCl ₄	7	66.0	137.5	50.5	31.5	282	31	-	-	-	-	-
	acetic media CCl ₄		55.5	110.0	13.0	42.5	420	108	78.0	100.0	100.0	100.0	78.0
-C≡N	acetic media CCl ₄	5 1/2	68.0	95.0	28.0	44.0	245	65	67.6	100.0	100.0	100.0	67.6

(※) after saponification if necessary

(**) acid value : 39.0. Other values are slightly wrong because amino group.

TABLE V

Influence of the solvent on the oxidation of methyl oleate with $(\text{AcO})_2\text{Hg}$
 (temperature : 90°C - reaction time : 14h. - molar ratio $(\text{AcO})_2\text{Hg}$ / fatty chain: 1 -
 concentration solvent/fatty chain : 5 cm³/g)

Assays	Analytical values										hydroxylation yie
	crude product			saponified product			from UV data after dehy-				
	iodine value	acetyl value	Hg bound: (g/100g)	hydroxyl value	UV data (E ₁ ¹) after dehydration	hydroxyl value	hydroxyl value	hydroxyl value	hydroxyl value	hydroxyl value	
acetic acid	74.0	114.0	1.3	133.0	600	42	70.7	70.9	70.9	70.9	70.9
ethyl oxide (*)	82.0	11.0	0.6	0	~ 0	~ 0	0	0	0	0	0
ethyl alcohol	19.5	135.0	26.5	0	~ 0	~ 0	0	0	0	0	0
benzene	28.0	157.0	23.8	27.0	149	15	14.3	18.0	18.0	18.0	18.0
carbon tetrachloride	28.0	161.0	25.5	24.5	135	15	13.2	16.5	16.5	16.5	16.5
acetic acid, benzene (**)	71.5	117.0	8.0	92.5	376	51	49.1	48.2	48.2	48.2	48.2
acetic acid, benzene (***)	51.5	147.0	19.5	54.0	242	0	28.6	26.6	26.6	26.6	26.6
dioxan	72.5	83.5	4.3	88.5	440	28	48.2	51.4	51.4	51.4	51.4
dioxan (****)	47.5	148.0	11.8	97.5	480	40	52.1	56.3	56.3	56.3	56.3
dioxan (*****)	67.0	123.0	3.6	140.5	698	49	74.8	82.1	82.1	82.1	82.1

(*) 40°C. (**) Acetic acid 3 cm³, benzene 2 cm³.

(***) Acetic acid 4.8 cm³, benzene 0.2 cm³.

(****) Molar ratio $(\text{AcO})_2\text{Hg}$ /methyl oleate = 2.

(*****) Molar ratio = 2 and reaction time 50 h. .

TABLE VI

$(\text{CH}_3\text{COO})_2\text{Hg}$ oxidation of functional derivatives of oleic chain

(temperature 90°C - reaction time 16 hrs. - molar ratio $(\text{CH}_3\text{COO})_2\text{Hg}/\text{fatty chains} = 1$ - solvent: acetic acid - concentration solvent/fatty chain: $5\text{cm}^3/\text{g}$)

A s s a y s	Analytical values*				Hydroxylation yields
	Iodine value	Hydroxyl value	UV data after dehydration (E_1^1) at $232\text{m}\mu$	at $268\text{m}\mu$	
- COOCH_3	81.0	128.0	600	42	66.3
- COOH	81.5	133.0	560	0	58.1
- CH_2OH	81.5	280.5	560	18	57.6
- $\text{CH}_2 - \text{OCOCH}_3$	80.5	278.5	522	39	55.5
- $\text{C} \equiv \text{N}$ **	80.0	137.2	528	45	57.0
- $\text{CH}_2 - \text{NH}_2$	81.5	202.1	585	38	60.8

* after saponification

** reaction time : 24 hrs.

TABLE VII

Characteristics and composition of an oxonation product

(methyl oleate - 160kg/cm² · p_{H₂} = p_{CO} - 150° - 1% Co - Co laurate)

Analytical characteristics

Acid value	80.0	→	1.43 millifonction/g
Ester value	167.0	→	2.98 mf/g
Hydroxyl value	18.0	→	0.32 mf/g
Carbonyl value	67.0	→	1.20 mf/g
Iodine value	0		

Functions repartition

Carbonyls free	1.43
combined	2.98
Alcohols free	0.32
combined	2.98
Carbonyls	1.20

Total :	8.91	Awaited 8.97
---------	------	--------------

Composition (% by weight)

Methyl stearate (by G.L.C.)		→	3.4
Lauric acid remaining	0.30 m.mole	→	6.0 %
Acid ester (1.43 - 0.30)	x 342	→	38.6
Aldehyde ester	1.20 x 326	→	39.1
Alcohol ester	0.32 x 328		10.5
		Total	97.6

Estolides : 100 - 97.6 = 2.4

TABLE VIII

Elimination of the catalyst in oxo crude products

(Methyl oleate - 160kg/cm² - P_{H₂} = P_{CO} - 150°C - Cobalt laurate)

Acid used	Solvent	Time (min.)	A n a l y t i c a l c h a r a c t e r i s t i c s *			
			Acid value	Ester value	Hydroxyl value	Carbonyl value
SO ₄ H ₂ 0.5 N	petroleum ether	130	64.0	165.0	18.0	69.0
SO ₄ H ₂ N	"	60	80.0	167.0	18.0	63.0
SO ₄ H ₂ 5 N	"	30	82.0	164.0	31.0	56.5
CH ₃ COOH	"	100	85.0	168.0	21.0	53.5
SO ₄ H ₂ N	T.H.F.	7	57.5	165.0	23.0	78.5
SO ₄ H ₂ N (progressively added)	"	75	41.5	168.0	26.0	93.5
(COOH) ₂	Et ₂ O	40	27.0	169.0	28.5	114.0

* iodine value = 0 for all assays.

TABLE IX

Influence of total initial gases pressure on oxonation of methyl oleate

(temperature: 150°C - p_{H₂} = p_{CO} - cobalt laurate - further treatment : N SO₄H₂ in THF)

pressure (kg/cm ²)	analytical values (*)						Composition (g/100g)						
	acid value	ester value	hydroxyl value	carbonyl value	acid- esters	alcohol- esters	aldehyde- esters	estolides	methyl stearate	alcohol- esters	aldehyde- esters	estolides	methyl stearate
80	74.5	171.0	30.0	61.0	35.0	18.0	35.5	0	9				
100	71.5	176.0	26.5	62.5	33.5	15.5	36.5	0	10				
120	49.0	161.0	21.0	83.0	19.5	12.5	48.0	3.0	11				
140	74.5	163.0	18.5	63.0	35.0	11.0	37.0	0	11				
160	41.5	168.0	26.0	93.5	15.0	15.0	54.5	0	10				
180	68.0	179.0	20.0	72.0	31.5	11.5	42.0	1.0	8				

(*) iodine value = 0 for all assays.

TABLE X

Influence of temperature on oxonation of methyl oleate

(total initial pressure : 160 kg/cm² - p_{H₂} = p_{CO} - cobalt laurate - further treatment :
N SO₄H₂ in THF)

Temperature (°C)	Analytical values (※)				Composition (g/100g)					
	acid value	ester value	hydroxyl value	carbonyl value	acid- esters	alcohol- esters	aldehyde- esters	estolides	methyl stearate	
130	57.0	177.0	29.0	64.0	24.5	17.0	37.0	0	8 (**)	
150	41.5	168.0	26.0	93.5	15.0	15.0	54.5	0	10	
170	18.5	177.0	57.5	50.0	1.0	34.0	29.0	26.0	4	
190	17.0	175.0	80.0	8.0	0	47.0	4.5	38.5	4	

(※) iodine value = 13 for assay n° 7, and = 0 for all other assays.

(**) methyl oleate 9.

TABLE XI

Influence of partial pressures on oxonation of methyl oleate

(total initial pressure : 160 kg/cm² - cobalt acetate - further treatment: oxalic acid in ether

tempe- rature (°C)	PH ₂ :pCO	reac- tion time (h.)	Analytical values (*)				Composition (g/100g) (**)					
			acid value	ester value	hydro- xyl value	carbo- nyl value	acid- esters	alco- hol- esters	aldéhy- de- esters	esto- lides	methy- stearyl	
150	4 : 1	26	7.5	178.5	25.0	79.5	4.5	15.0	46.5	21.0	13	
	2 : 1	19	9.0	179.0	43.0	107.0	5.5	25.0	62.5	0	10	
	1 : 1	37	9.0	182.0	34.0	123.0	5.5	20.0	71.5	0	7	
	1 : 2	54	13.0	179.0	28.0	126.0	8.0	16.5	73.5	0	5	
190	1 : 4	122	6.5	180.0	20.5	126.0	4.0	12.0	73.5	0	4	
	4 : 1	19	0	180.0	84.5	8.5	0	49.5	5.0	34.5	11	
	2 : 1	20	0	177.0	80.0	9.0	0	47.0	5.0	42.0	6	
	1 : 1	40	2.0	180.0	84.0	19.0	1.5	49.0	11.0	34.5	4	
190	1 : 2	72	0	178.0	62.0	32.5	0	36.5	19.0	39.5	5	
	1 : 4	37	13.0	179.0	23.0	89.0	8.0	13.5	52.0	0	13	

(*) iodine value = 13.5 for assay n° 18, 28.5 for assay n° 23 and 0 for all others.

(**) methyl oleate 9.0 for assay n° 18 and 17.0 for assay n° 23.

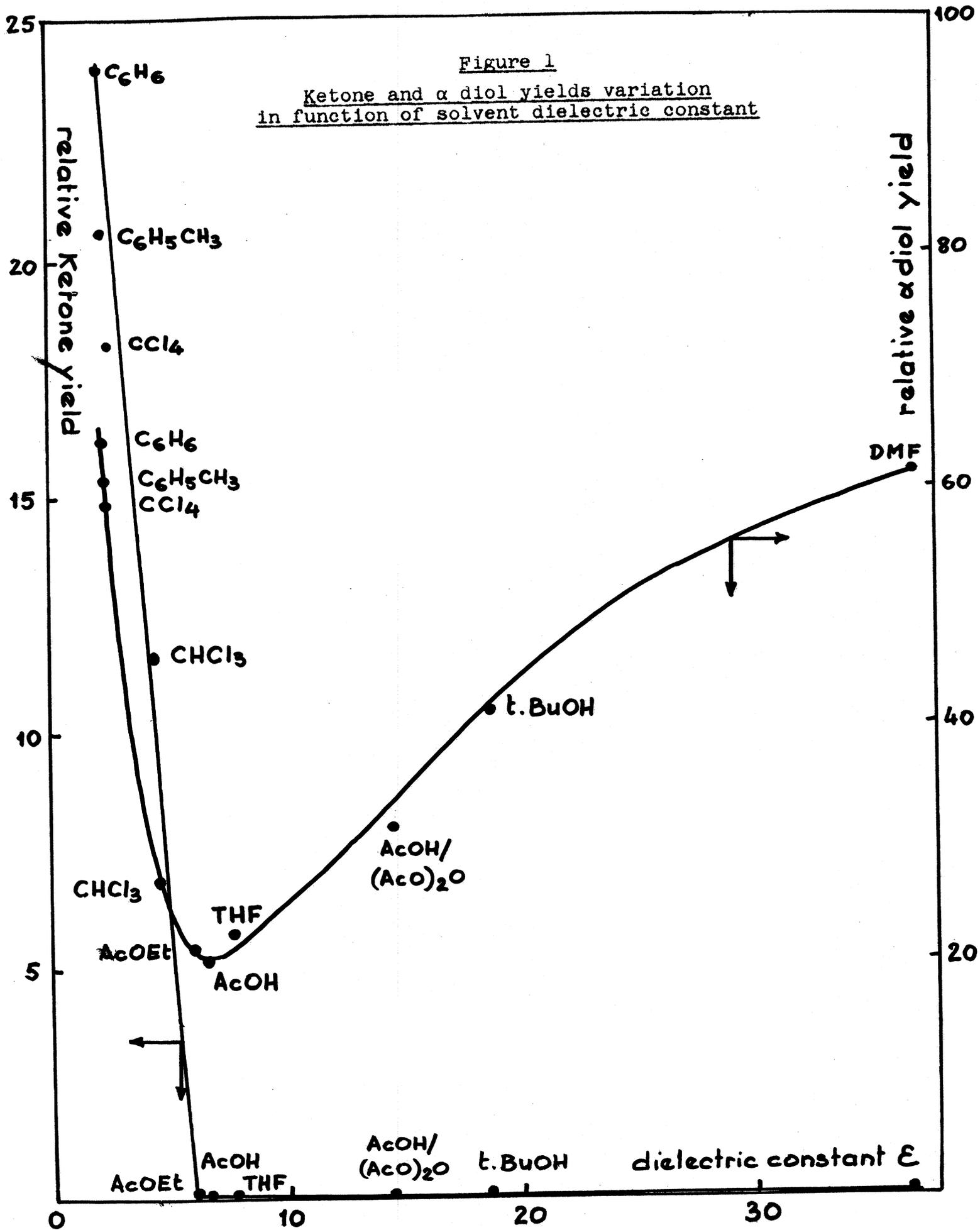
TABLE XII

Influence of cobalt: proportion on oxonation of methyl oleate

(total pressure : $160\text{kg/cm}^2 - P_{\text{H}_2} = P_{\text{CO}}$ - Cobalt generator: $(\text{AcO})_2\text{Co}$ - Destruction oxalic acid

Temperature °C	Co/OlMe g/100g	Reaction time (mn)	Acid esters	Composition g/100g *			Methyl stearate	Estolide
				Alcohol esters	Aldehyde esters			
150	0.1	203	7.0	10.0	79.0	8.0	0	
	0.2	89	7.0	10.0	79.5	7.0	0	
	0.5	55	8.5	11.5	73.5	10.0	0	
	1	37	5.5	20.0	71.5	7.0	0	
	2	20	12.5	22.0	55.5	13.0	0	
190	0.1	133	2.5	40.5	29.5	5.0	22.5	
	0.2	116	1.0	45.5	15.5	4.0	34.0	
	0.5	117 (?)	0	55.5	5.0	5.0	34.5	
	1	40	1.5	49.0	11.0	4.0	34.5	
	2	38	0	54.5	0.0	4.0	41.5	

* no more methyl oleate present.



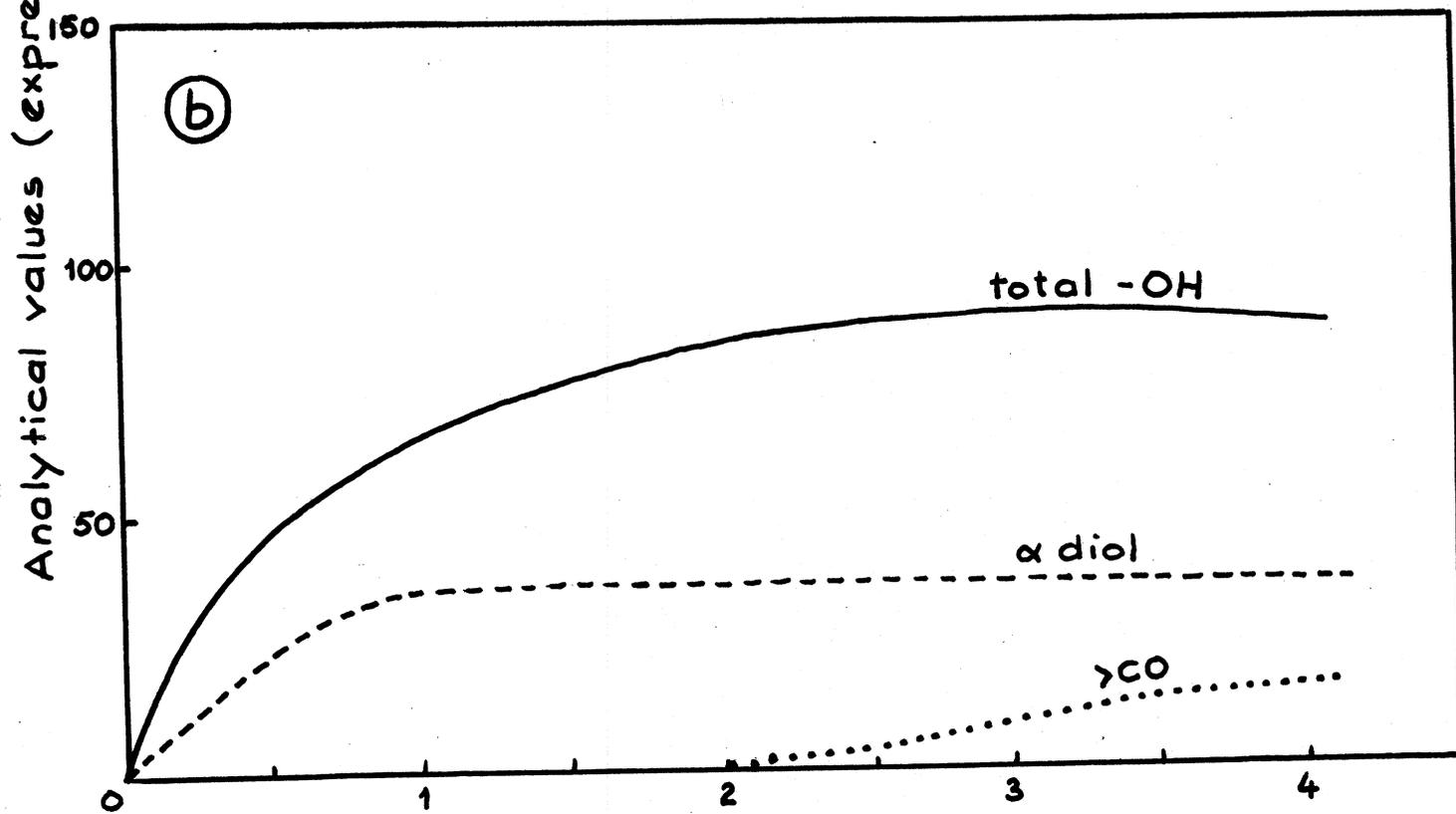
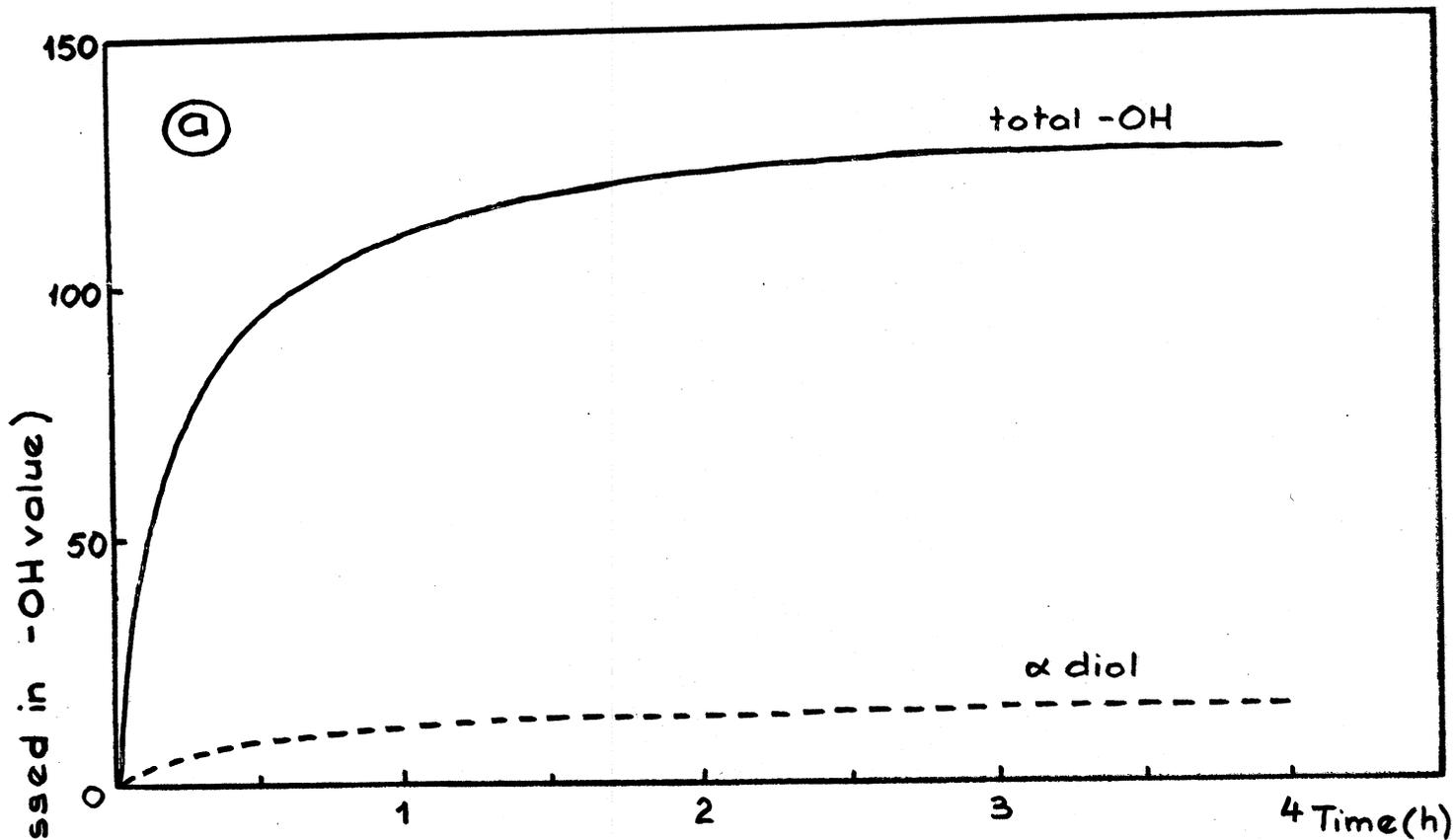
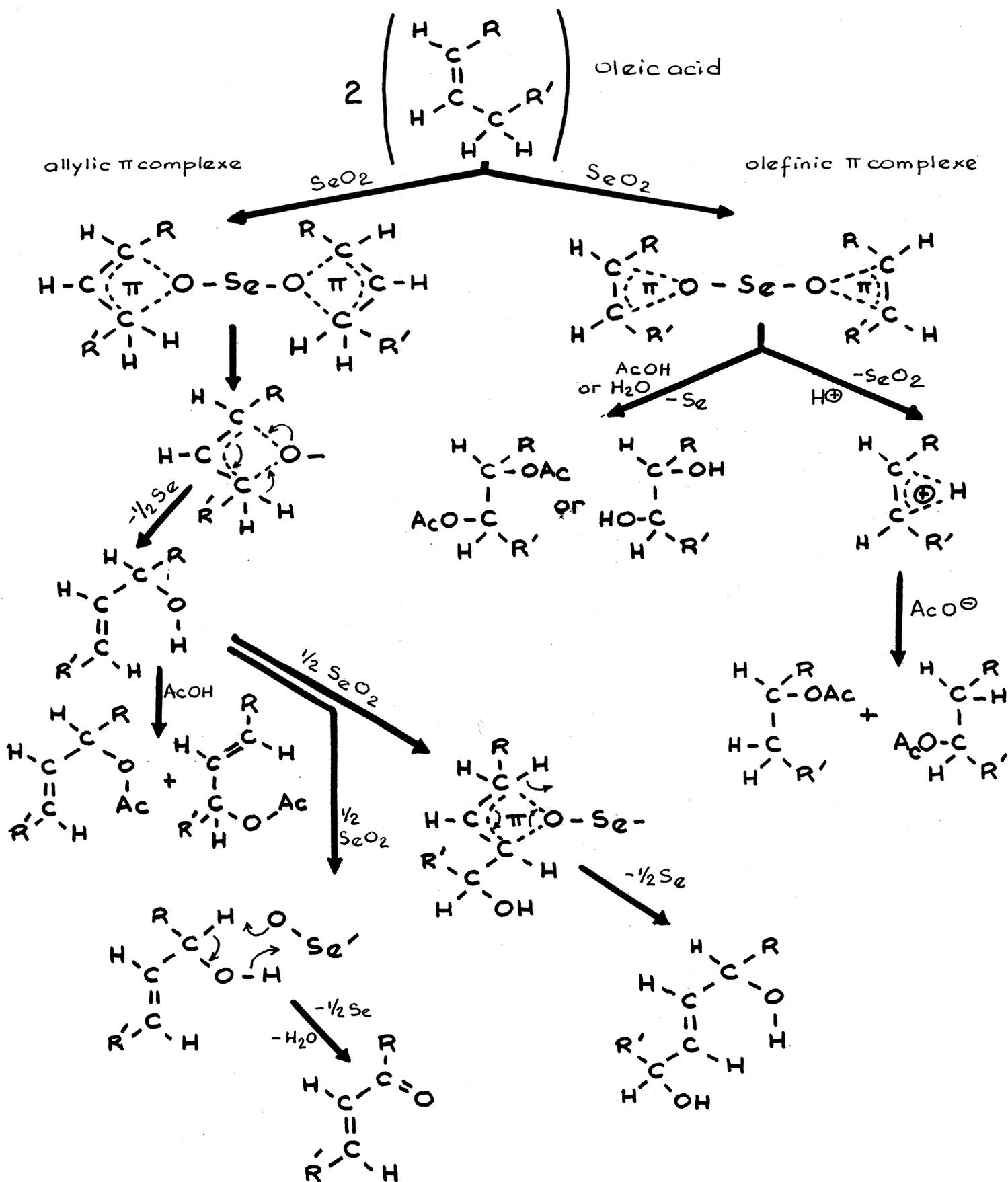


Figure 2

Kinetics of oxidation

Figure 3 - SeO_2 oxidation mechanism of oleic chain



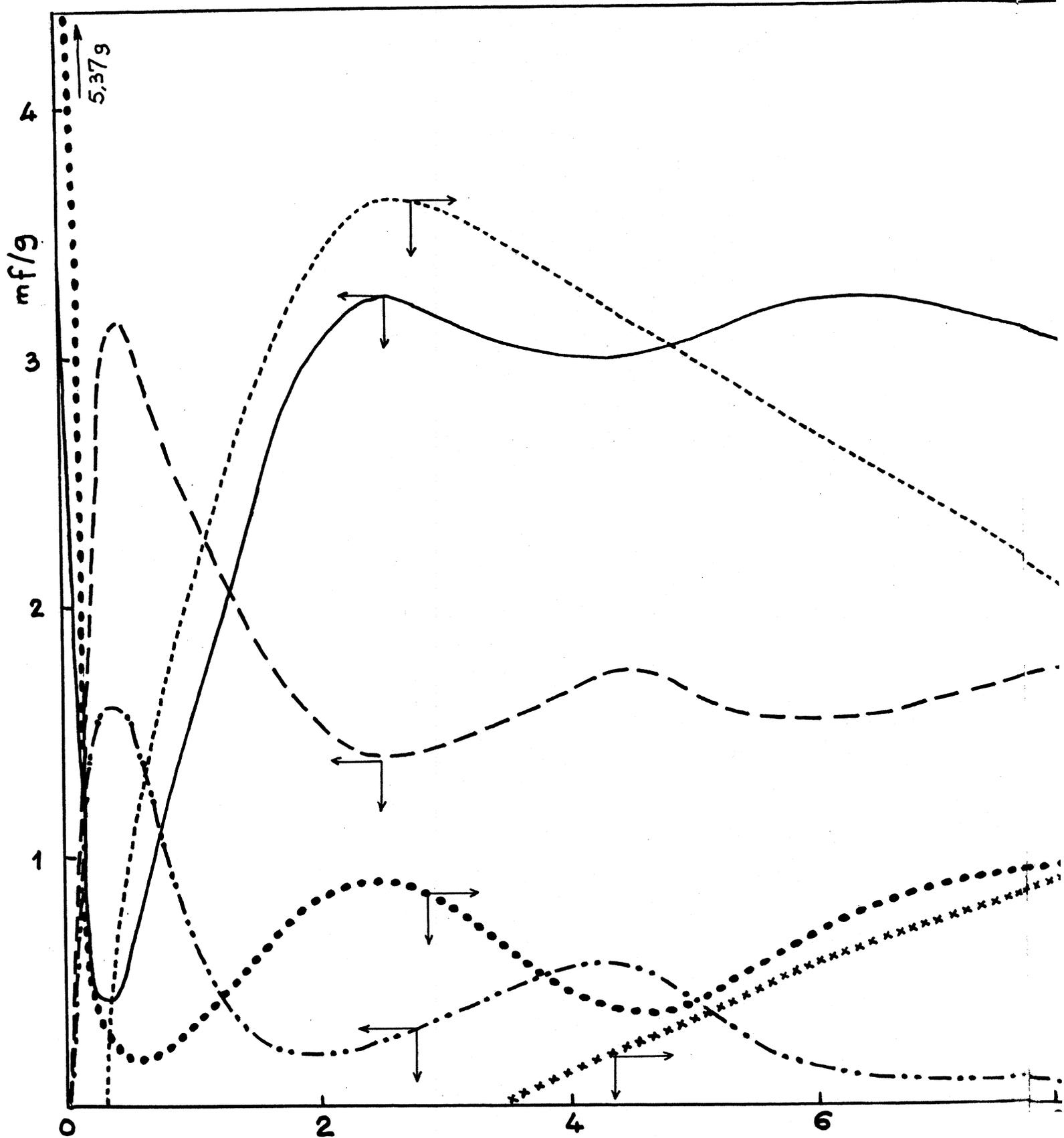
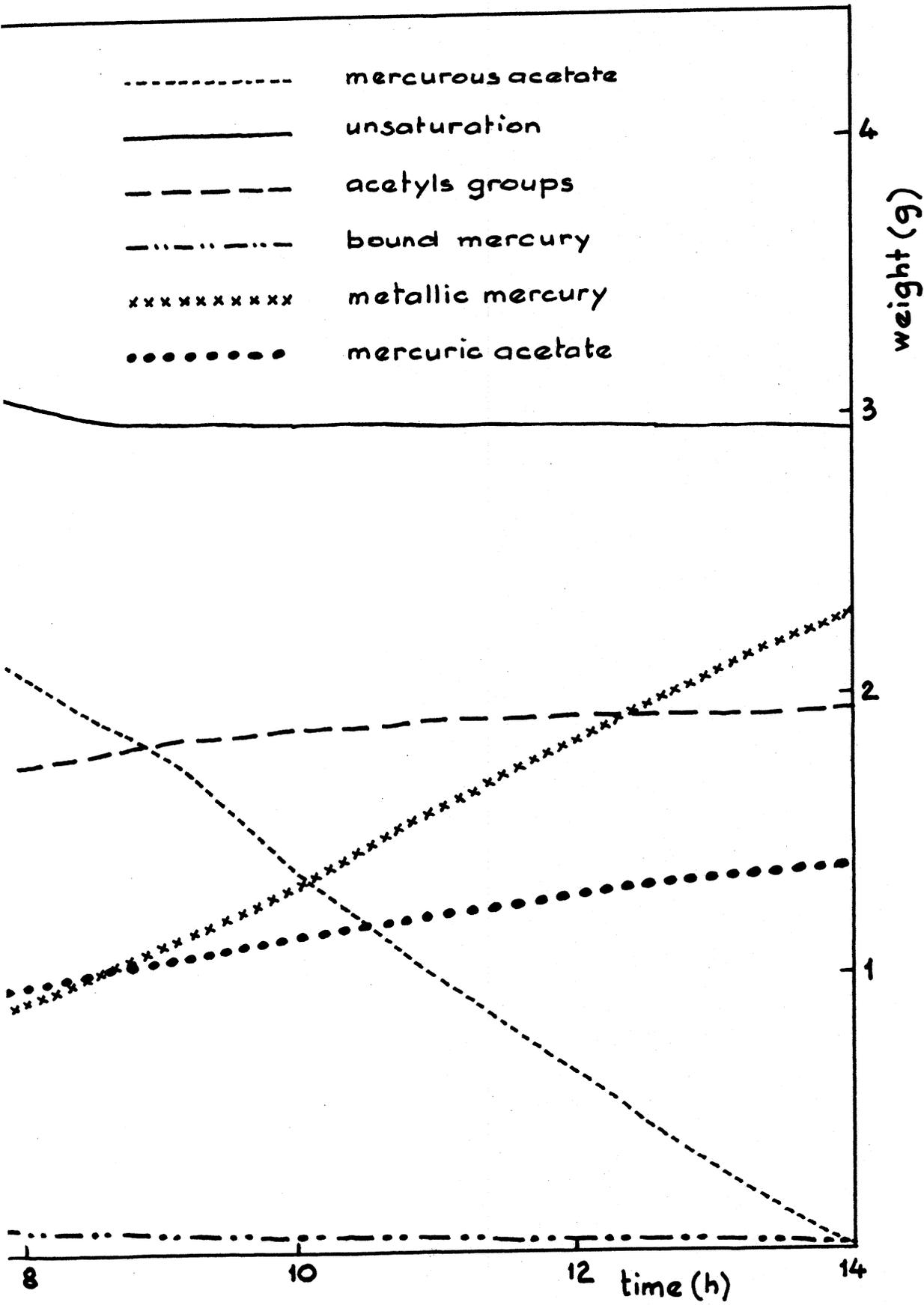
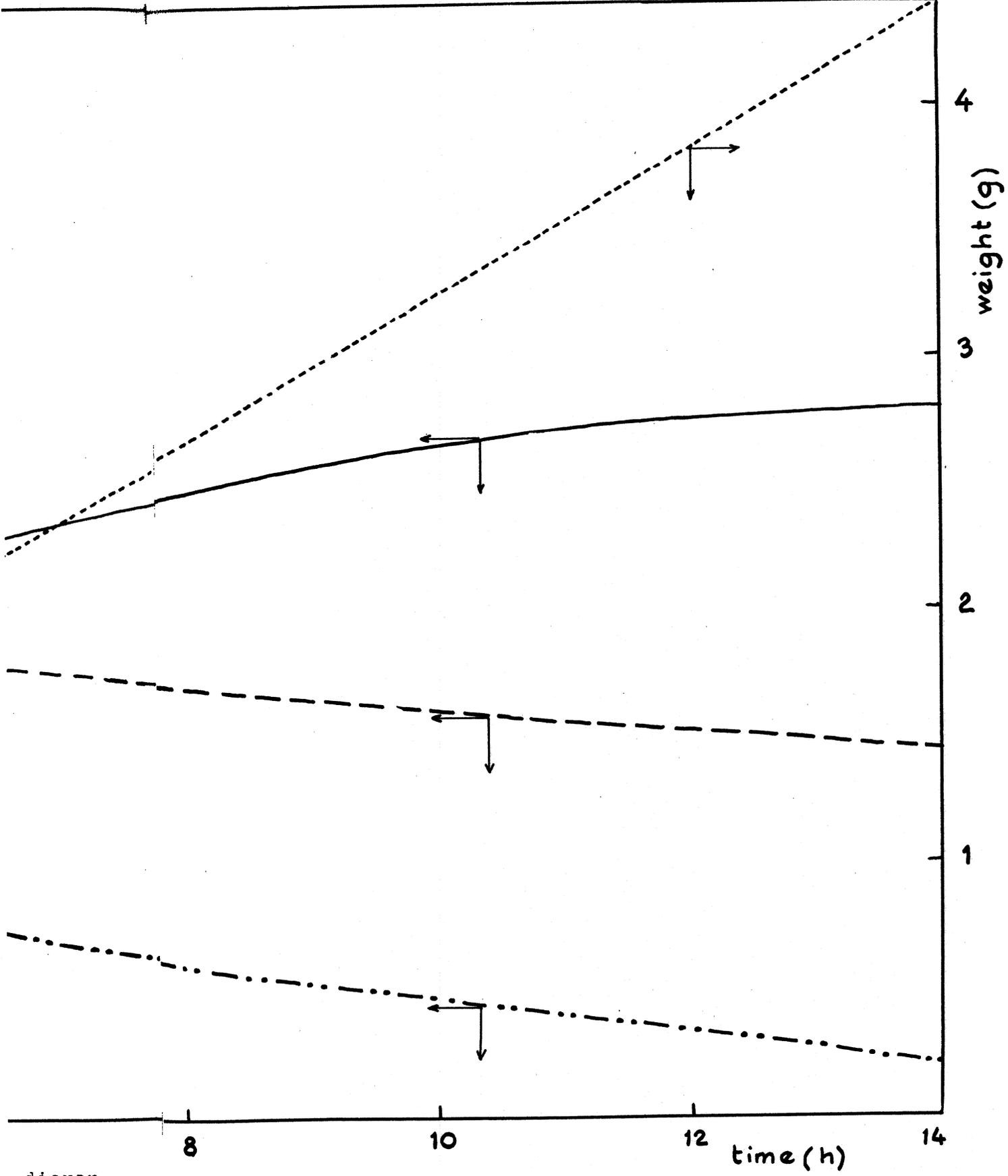


Figure 4 - Kinetic of $(AcO)_2Hg$ oxidation of methyl oleate in acetic acid

- mercurous acetate
- unsaturation
- - - - - acetyls groups
- · - · - · - bound mercury
- xxxxxxxxxx metallic mercury
- mercuric acetate





dioxan

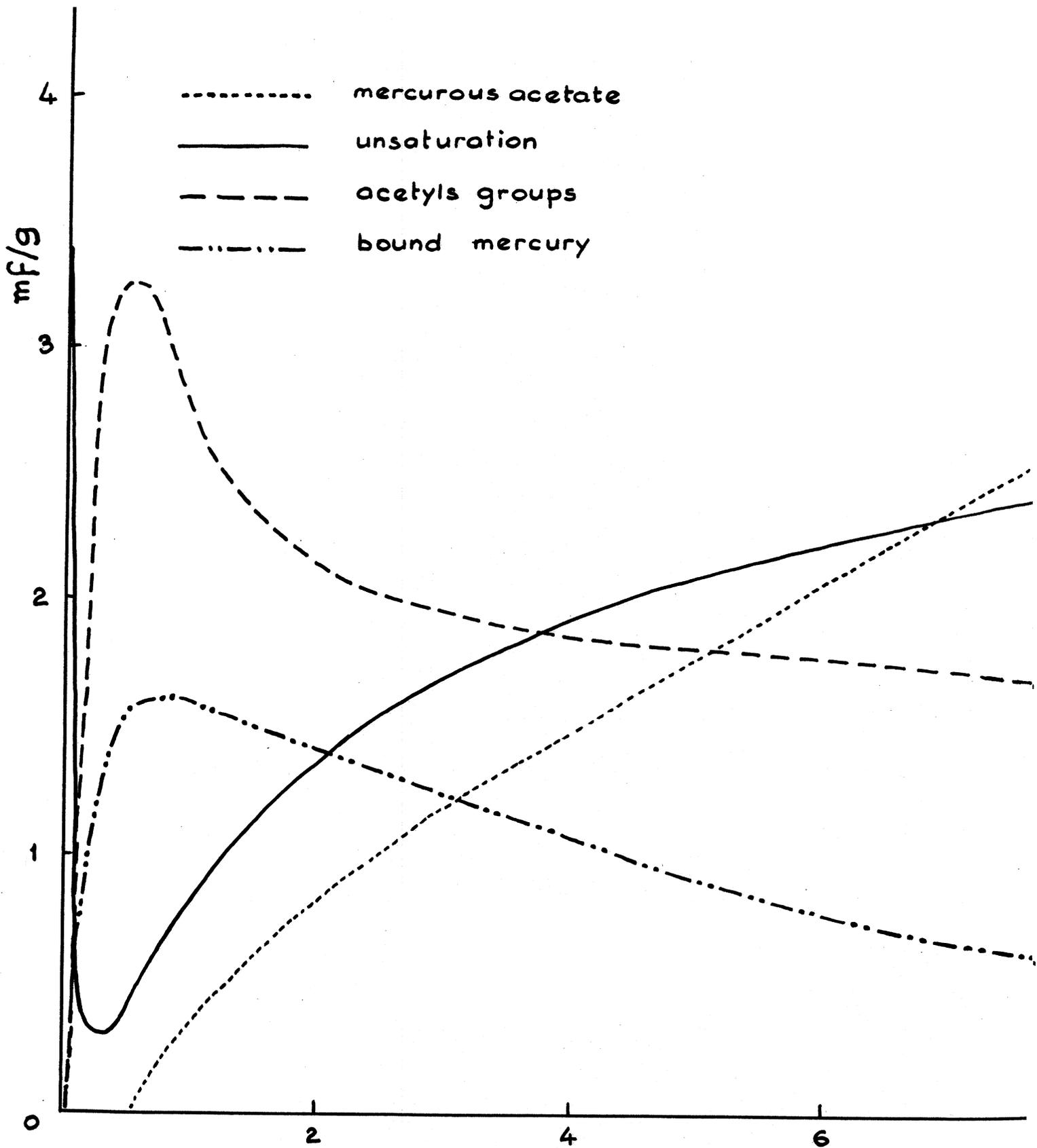
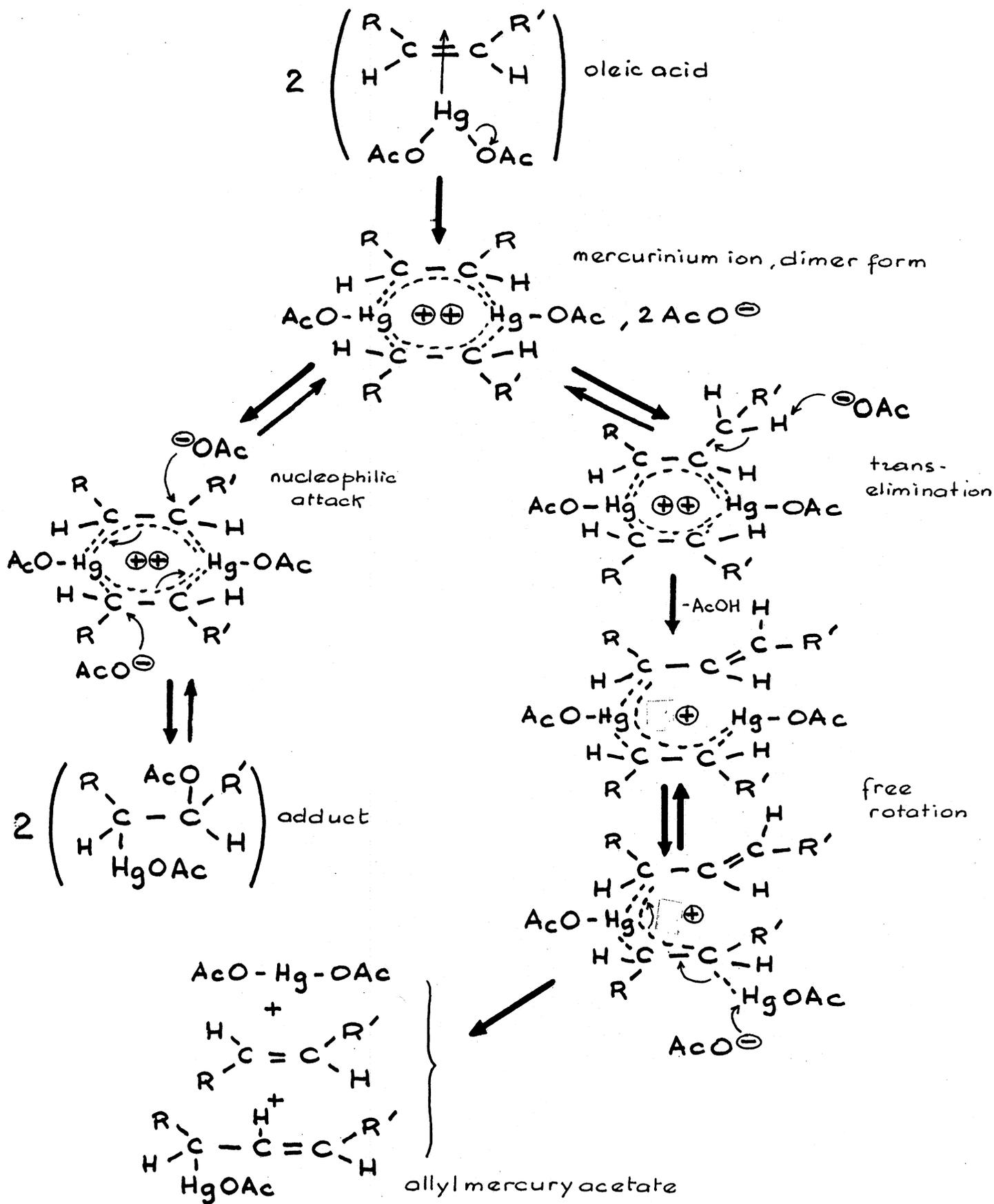
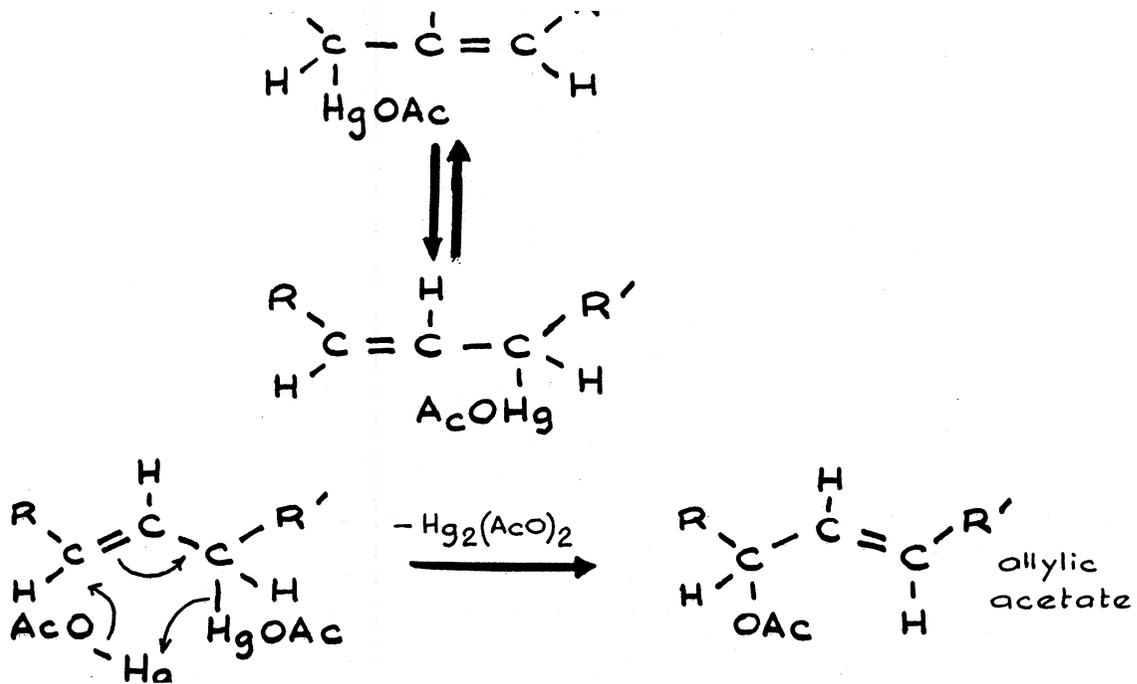


Figure 5 - Kinetic of $(AcO)_2Hg$ oxidation of methyl oleate in dioxan

Figure 6 - Mercuric acetate oxidation mechanism of oleic chain





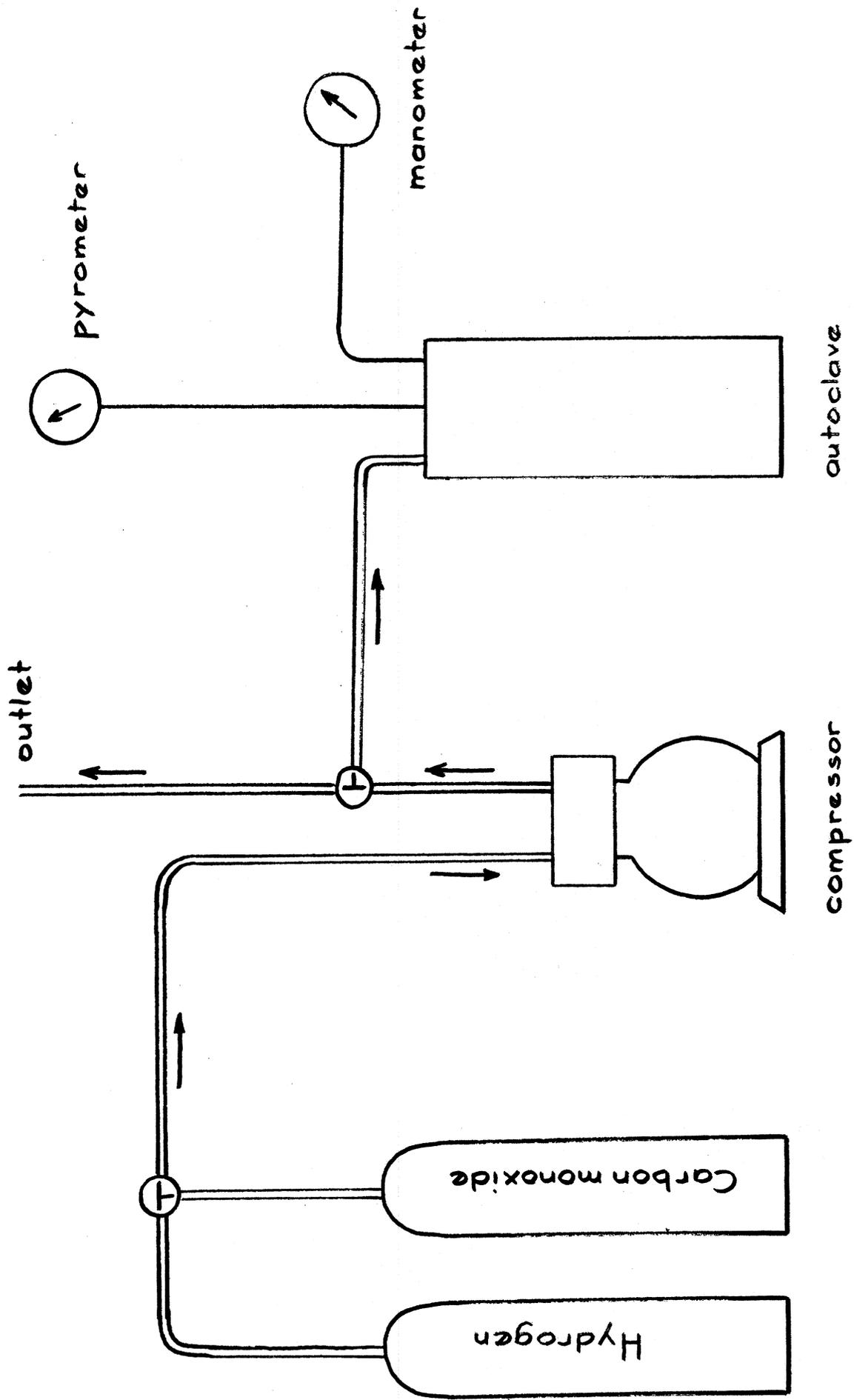


Figure 7 - Oxonation apparatus

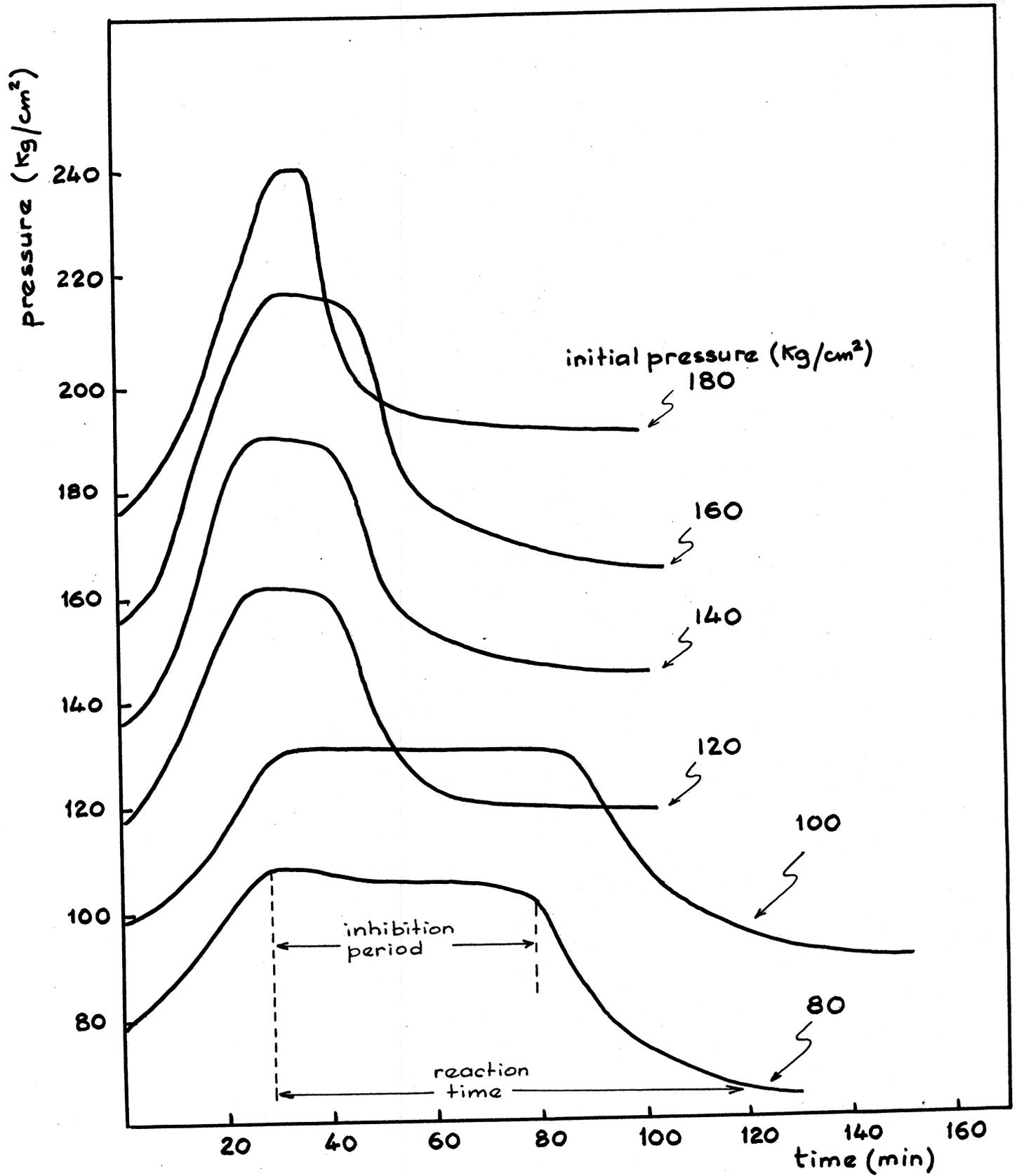


Figure 8 - Variation of pressure in function of initial pressure

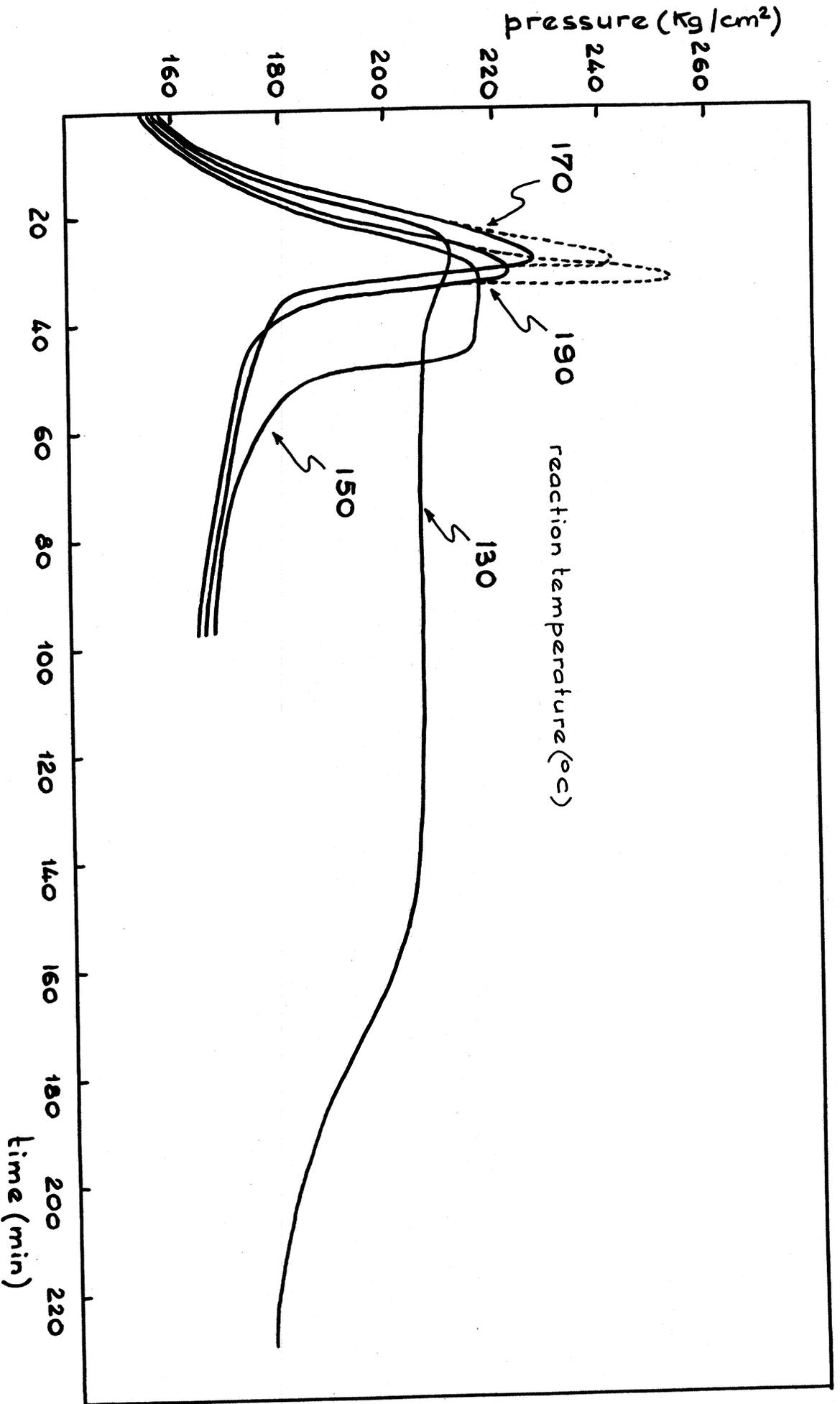


Figure 9 - Variation of pressure in function of temperature

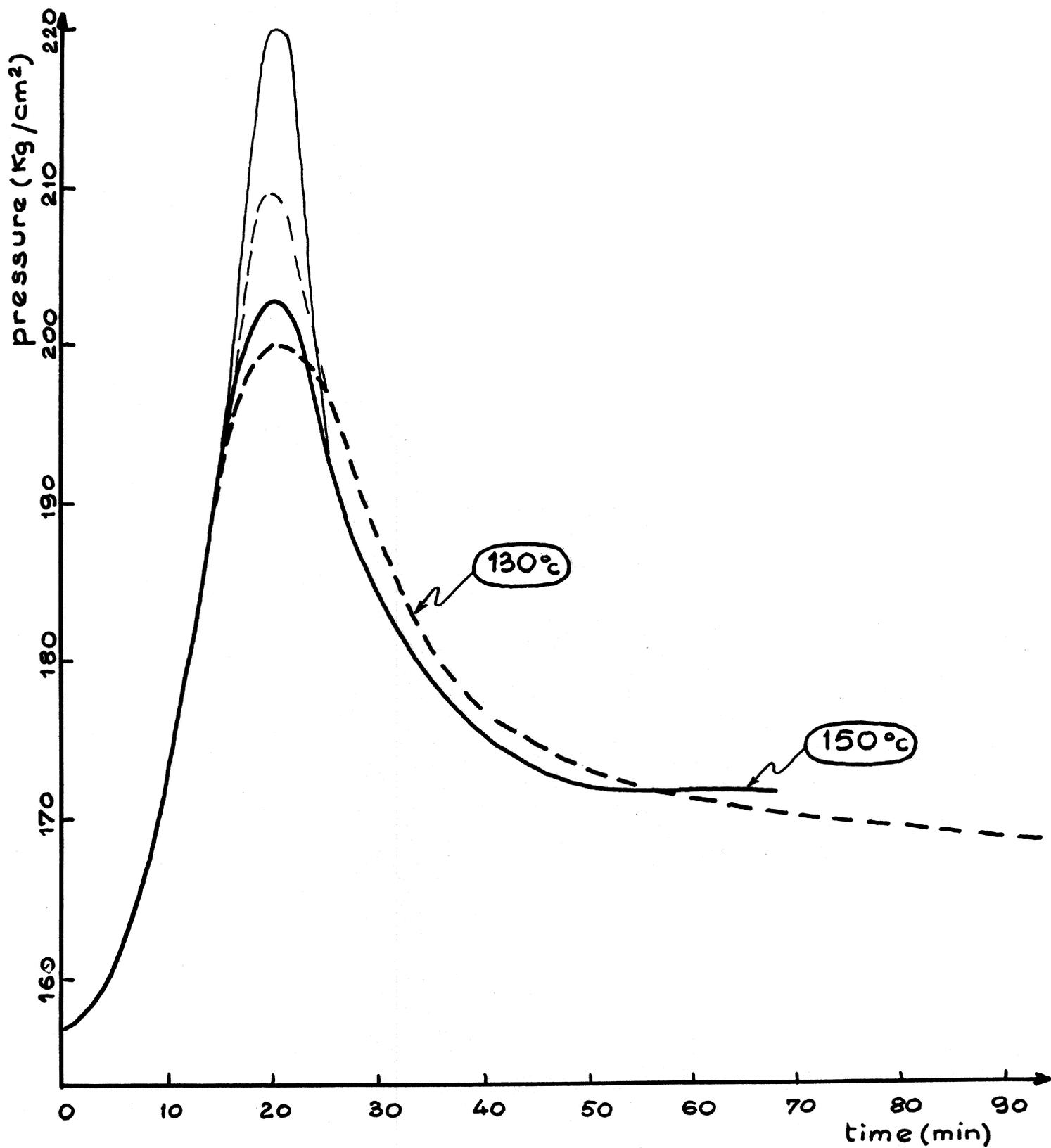


Figure 10 - Oxonation with $\text{Co}_2(\text{CO})_8$
Variation of pressure as a fonction of time

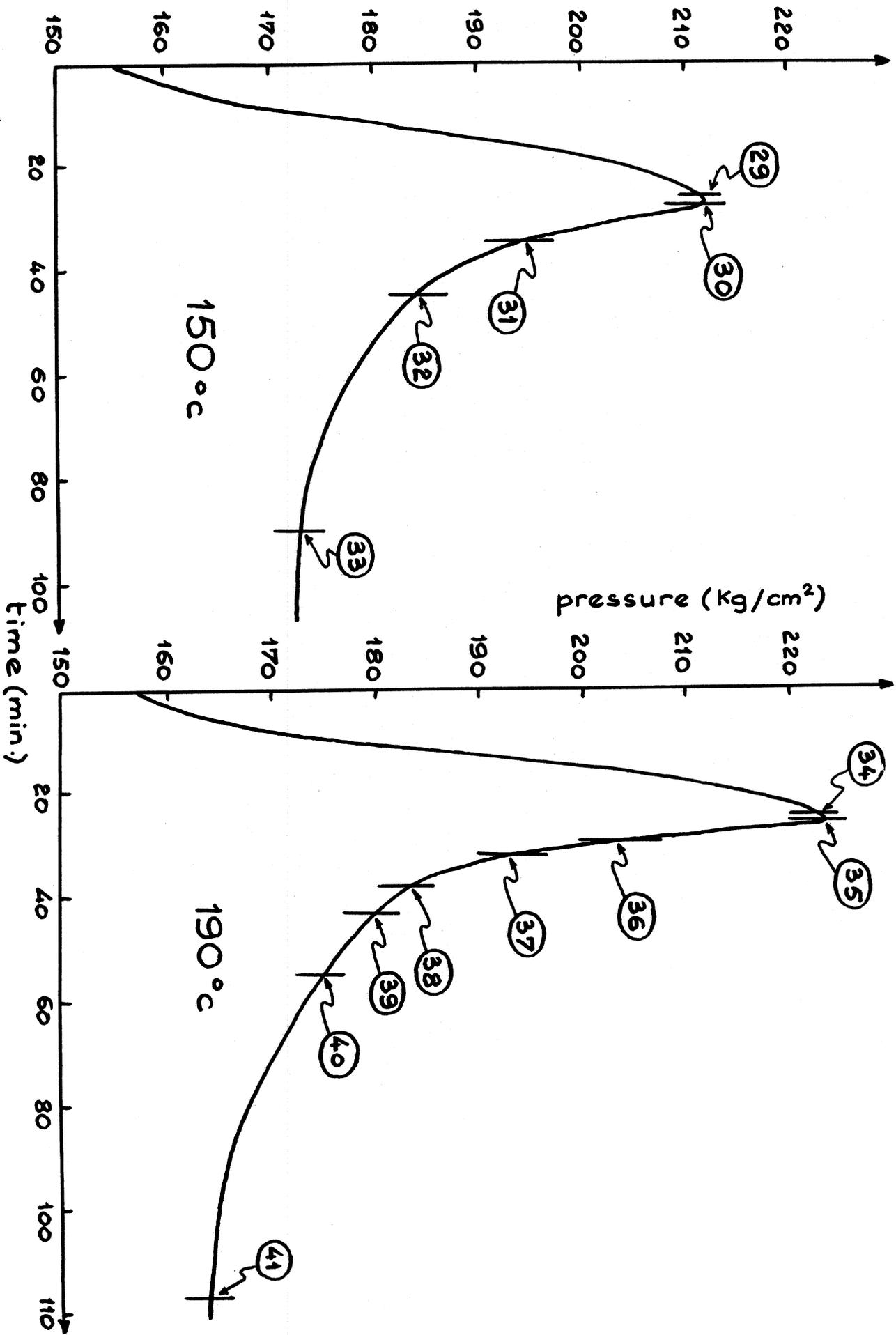
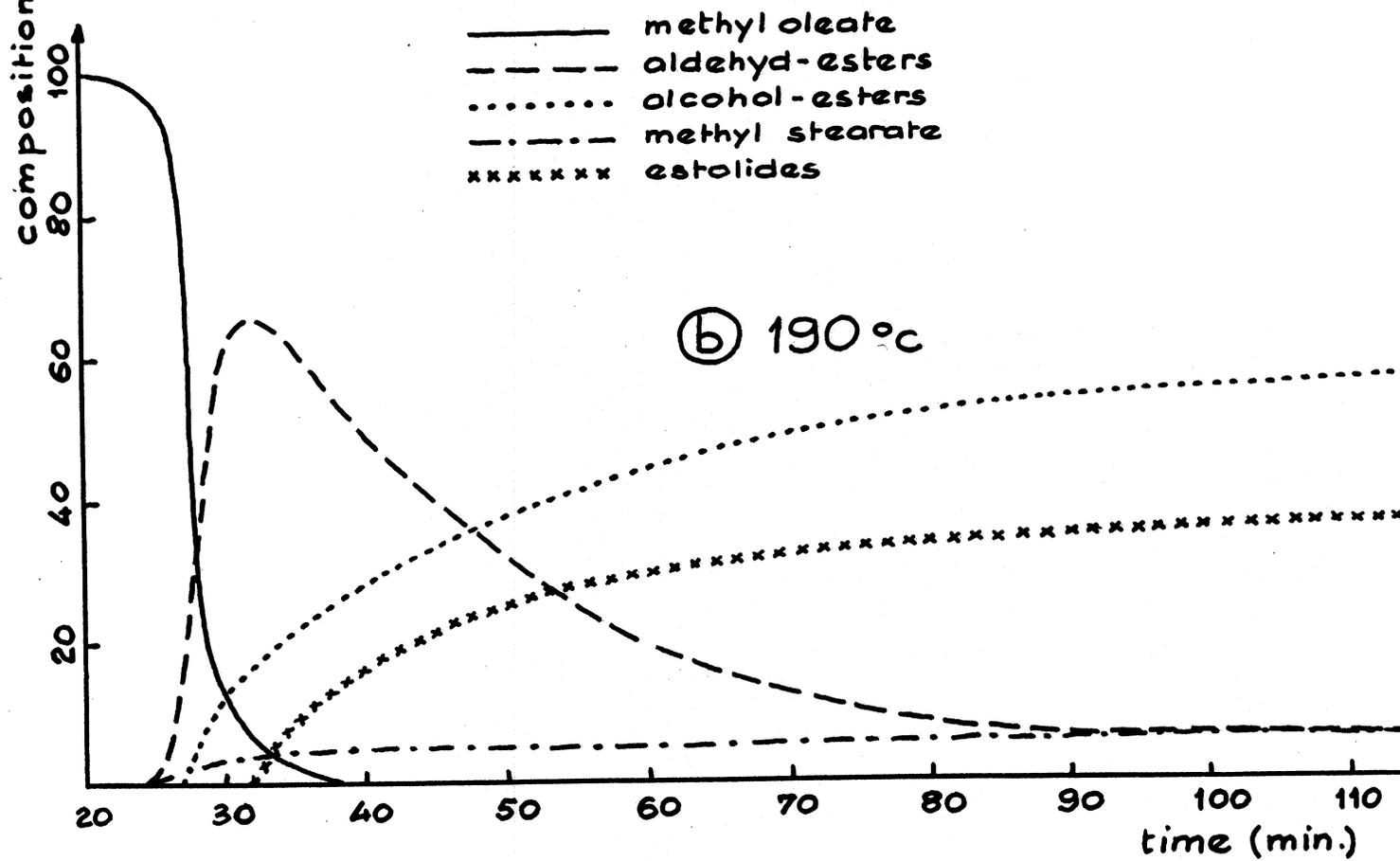
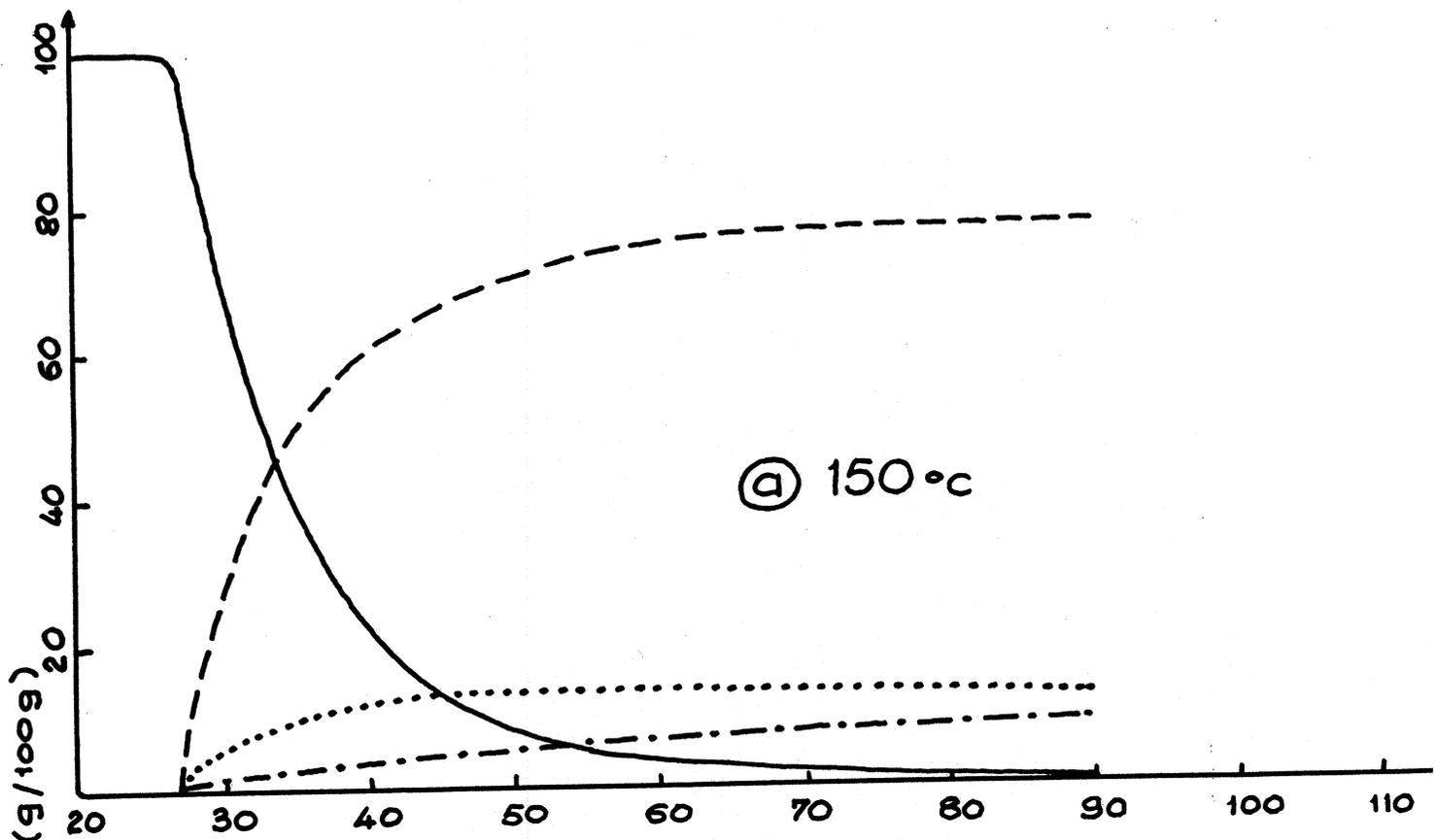


Figure 11 - Curves for kinetic study of the oxoreaction



- methyl oleate
- - - aldehyd-esters
- alcohol-esters
- . - . methyl stearate
- ***** estolides

Figure 12 - Kinetic curves of oxoreaction